



PROTON INDUCED X-RAY EMISSION-

mass calibration, computer analysis and applications to
work environment aerosols

GERD JOHANSSON

1981



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Organization LUND UNIVERSITY	Document name DOCTORAL DISSERTATION
Department of Nuclear Physics Sölvegatan 14	Date of issue August 21, 1981
S-223 62 LUND, Sweden	CODEN: LUTFD2/(TFKF-1001)/1-111 /(1981)
Author(s) Gerd Johansson	Sponsoring organization

Title and subtitle
Proton Induced X-Ray Emission - Mass Calibration, Computer Analysis and Applications to Work Environment Aerosols.

An experimental arrangement for fast and reliable analysis by Particle Induced X-ray Emission (PIXE) has been designed and the feasibility of using a general mass calibration procedure demonstrated. The accuracy and the long-term stability of the calibrated system has been shown to be better than 5% and 2.5% respectively for thin homogeneous samples. Experimental arrangements and a procedure for the simultaneous use of proton induced γ -rays from the $^{19}\text{F}(p,\alpha\gamma)^{16}\text{O}$ -reaction for fluorine analysis have also been developed and tested. To reduce charge build-up in thick insulating samples, an arrangement with a hot carbon filament emitting electrons was designed and included in the set-up, thereby extending the usefulness of PIXE. Improvements in the computer program HEX for resolving PIXE-spectra have been made, e.g., by including routines handling escape peaks and pile-up peaks. Escape ratios in the energy interval 3.3-10.6 keV have been measured with good accuracy and included in HEX.

The welding fumes from thirteen electric arc welding processes have been characterized. The total fume emissions and elemental compositions of the fumes have been measured. The particle size distributions of different elements were determined by the use of a combination of cascade impactors and PIXE-analysis. The mass median aerodynamic diameters of the size-distributions were less than $1\text{ }\mu\text{m}$. The relative abundance and solubility of hexavalent chromium (Cr(VI)) was measured in the fume from welding of stainless steel.

Key words

Classification system and/or index terms (if any)

Supplementary bibliographical information

Language
English

ISSN and key title

ISBN

Recipient's notes

Number of pages

Price

Security classification

Distribution by (name and address)

Department of Nuclear Physics
Sölvegatan 14
S-223 62 LUND, Sweden

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PROTON INDUCED X-RAY EMISSION - MASS CALIBRATION, COMPUTER ANALYSIS
AND APPLICATIONS TO WORK ENVIRONMENT AEROSOLS.

by

GERD JOHANSSON

Summary	IX
Acknowledgements	XVI
I. "A Facility for Multielemental Analysis by PIXE and the $^{19}\text{F}(\text{p}, \alpha\gamma)^{16}\text{O}$ Reaction", LUTFD2/TFKF-3027 (1981) - submitted for publication to The Journal of Radioanalytical Chemistry, (in collaboration with Klas Malmqvist and Roland Akselsson)	1
II. "Calibration and Long-Term Stability of a PIXE Set-up", Nucl. Instr. Meth. <u>181</u> (1981), 81, (in collaboration with Jan Pallon, Klas Malmqvist and Roland Akselsson)	31
III. "Elimination of Charging in the Proton-Induced X-Ray Emission Analysis of Insulating Samples", Nucl. Instr. Meth. <u>131</u> (1975), 377, (in collaboration with Mats Ahlberg and Klas Malmqvist)	39
IV. "Modifications of the HEX Program for Fast Automatic Resolution of PIXE-Spectra", LUTFD2/TFKF-3028 (1981) - submitted for publication to X-Ray Spectrometry.	43
V. "Characteristics of Welding Fumes", LUTFD2/TFKF-3030 (1981), (in collaboration with Klas Malmqvist, Mats Bohgard and Roland Akselsson)	63

SUMMARY

The first experiments demonstrating the analytical method Particle Induced X-ray Emission (PIXE) were performed at our laboratory in 1970 (ref. 1). The method has now spread all over the world and is used by more than 200 different laboratories. Two international conferences at Lund in 1976 and 1980 (refs. 2 and 3) have demonstrated its capability and usefulness in different applications.

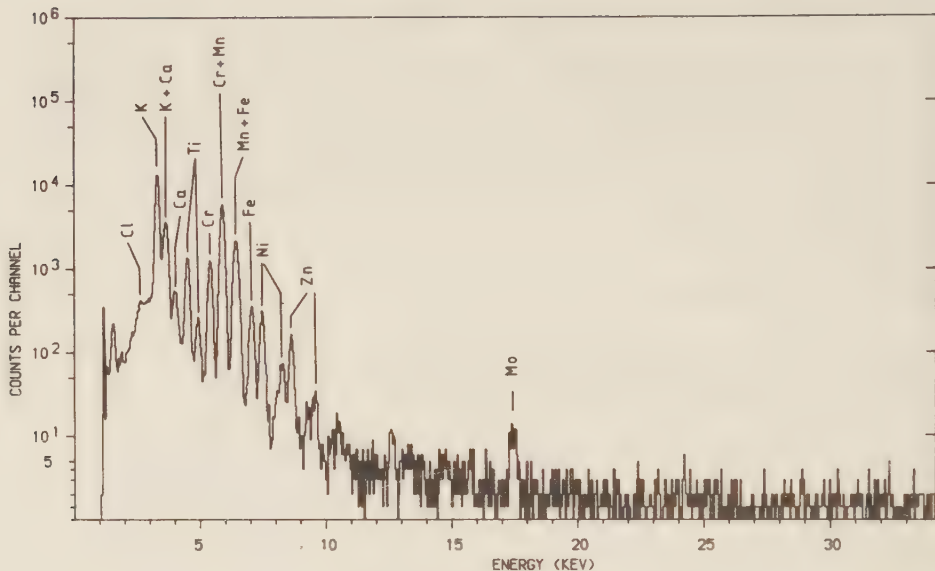
The aims of this work were:

- 1) to develop a PIXE-system, which will perform fast and accurate multi-elemental analyses of unknown samples and
- 2) to apply the PIXE-method to an important problem, the characterization of welding aerosols, in which the capability of the method can be fully utilized.

The PIXE-method

When a charged particle (normally a proton or an alpha-particle) with an energy of 1-4 MeV/u hits a sample, there is a large probability for the creation of a vacancy in one of the inner atomic shells. When the vacancy is filled, either an X-ray or an Auger electron is emitted. The energy of the X-ray is characteristic of the element from which it originates and it can be detected with a solid state detector. By counting the number of X-ray pulses of a certain energy and integrating the total number of particles hitting the sample, the mass of the element producing the X-rays detected can be calculated.

Suitable electronics are used to amplify the signals from the X-ray detector and a pulse height spectrum (see figure) is stored in a multichannel analyser. In the Lund set-up, the spectra are transferred to magnetic tape and, for the evaluation of the masses of the different elements, a special computer code is used. Modifications of the computer program to improve the accuracy of spectrum evaluation are described in paper IV.



PIXE is a fast multi-elemental method. A quantitative analysis of all elements heavier than phosphorous is obtained and the irradiation time for routine analysis is normally 1-3 minutes. The detection limits obtained in such routine analysis are in the ng-range for all the elements. Another advantage which makes the PIXE-method unique is that very small samples ($\sim 10 \mu\text{g}$) can be analysed. The accuracy and precision for thin samples ($< 1 \text{ mg/cm}^2$) are better than 5 % (see paper II). PIXE is an absolute method and the content of the sample can be quantified routinely without using standard samples. At our laboratory standard samples are, however, used for the initial mass calibration of the experimental set-up (see paper II).

Due to absorption of the X-rays from the lighter elements in the material between the sample and the detector, only elements heavier than phosphorous can

be analysed quantitatively. An advantage of PIXE, as compared to other X-ray methods, is the possibility of simultaneously using nuclear reaction products including the elastic scattering of the incident particle for analysing lighter elements. In paper I, a method for determining fluorine in thin samples by detecting the γ -rays from the nuclear reaction $^{19}\text{F}(p,\alpha\gamma)^{16}\text{O}$ is described.

When analysing thick samples with the PIXE-method, the slowing-down of the particles and absorption of the X-rays in the sample have to be accounted for. Different solutions to the problem thus introduced for thick insulating samples are described in paper III.

The PIXE-method is at present used for many different kind of samples such as aerosol samples, biological samples, water samples and geological samples. At our laboratory, a main application has been the analysis of aerosol samples, i.e., particles collected on filter surfaces or thin plastic films. It has been demonstrated (ref. 4) that these samples are very well suited for PIXE-analysis since no sample preparation is required. Both ambient and occupational aerosols have been studied. The property of PIXE of being able to analyse very small samples is used when fractionating the aerosols into different particle sizes. Particle size is an important parameter in judging hygienic effects from inhalation of aerosols. In paper V, a characterization of fumes from different types of welding has been carried out.

Paper I

The first paper describes the experimental arrangement for PIXE-analysis developed in Lund. To be able to use it both for routine analysis, taking account of the specific advantages of PIXE, and for research work the constructed irradiation chamber is fairly large and complex.

The size of the beam (protons, 2.55 MeV) hitting the sample is selected by using a suitable collimator and beam homogeneity is obtained by a thin diffuser foil. After passing an exchangable filter which absorbs the low energy component the X-rays emitted from the sample are detected by a solid state detector ($\text{Si}(\text{Li})$). Both the absorber and the collimator can be changed externally and they are prepared for automatic control. An automatic system for sample changing is also

employed. To quantify the results, the proton current is measured. The performance of the beam, the current integration and the detector have been carefully tested to optimize the analytical conditions. On-demand beam pulsing is also implemented (ref. 5) to reduce pile-up effects in the spectrum and sample deteriorations due to heating. Detection limits and the accuracy and precision of routine analyses are also reported.

A routine for simultaneous detection of the X-rays produced and γ -rays from the reaction $^{19}\text{F}(p,\alpha\gamma)^{16}\text{O}$ for fluorine determination has also been developed. Fluorine, which is found in many different types of welding fumes, is important because of its hygienic effects. Its γ -rays of energies 6.13, 6.92 and 7.12 MeV are detected in a NaI crystal and the routine detection limit for F is about 100 ng/cm².

Paper II

An important feature of the PIXE-method is the possibility of quantitative analysis without using standards. A well calibrated system is however, required. In Paper II, an accurate calibration procedure of a PIXE set-up is described. For the calibration, commercially available thin homogeneous standard foils are used. The parameters of a physical model describing the system are then fitted to determine a calibration curve which is in agreement with the standard measurements. By using the calibration procedure suggested, errors due to incorrect standards can be decreased. The error can be further decreased by correcting for inhomogeneities in the standard foils. The accuracy of a set-up calibrated with the suggested procedure (e.g., the Lund set-up) is estimated to be better than 5 %.

To secure good long-term stability of the experimental arrangement and thus maintain a high quality of analysis, frequent controls must be made. A sample consisting of a thick silver plate with a copper spot in its centre was designed. This sample, which is very sensitive even to small changes in the set-up, is used to check the long-term stability. For the PIXE arrangement in Lund, the long-term stability is 2.5 % for a homogeneous sample and 4 % for a spot (inhomogeneous) sample.

Paper III

The high sensitivity of the PIXE-method depends partly on a relatively low continuous background radiation. When analysing thick highly-insulating samples, the background is increased significantly because of additional bremsstrahlung. The bremsstrahlung originates from electrons accelerated towards the positively charged sample. The sensitivity is also reduced as is the current to compensate for the higher count rate from the increased background.

In this paper, two different solutions of this problem are presented:

- 1) Electrons from a battery operated filament are sprayed on to the sample, thus avoiding charge build-up.
- 2) Higher pressure in the the vacuum chamber prevents charge build-up.

The first method using an "electron gun" is normally to be preferred to the second, since residual gas in the chamber may be a source of impurities and also increase the probability of leakage currents.

Paper IV

A fast and accurate computer program is necessary to make use of the high capability of the PIXE-method. The development of the program HEX by Kaufmann et al. (ref. 6) permitted great progress in this field. It was mainly developed for the fast resolution of PIXE-spectra from thin samples of ambient aerosols. Paper IV describes modifications to this computer program to extend its usefulness and improve the accuracy for other types of samples.

The sizes of the escape peaks relative to their parent peaks have been measured in the energy interval 3.3-10.6 keV. The values found are in good agreement both with theoretical calculations and other measurements reported in the literature. The computer code has been modified so as to be able to include the escape peaks in the physical model describing a PIXE-spectrum.

The time needed to analyse a sample can often be further decreased by increasing the count rate. This will, however, give rise to larger pile-up peaks in the spectrum. The pile-up peaks can be reduced by using suitable electronics for pile-up rejection or an on-demand beam system (ref. 5). Even with a well-working system for reducing the pile-up peaks, there will still be residual pile-up peaks in the spectrum. A special routine for fitting these peaks has been included in the HEX program. The routine is independent of constant count rate during sample irradiation and of a known pile-up interval.

Paper V

The fumes produced from electric arc welding have been characterized. Altogether thirteen different welding situations have been studied. The sampling has been performed in a specially designed welding chamber. The total emission and the elemental composition of the fume have been measured. In addition the sizes of the particles, which are very important parameters from the hygienic point of view, are determined using a cascade impactor.

To evaluate the health hazards of the fumes from stainless steel welding, it is important to be able to distinguish between Cr(III) and Cr(VI) since the latter has been shown to be carcinogenic. A combination of different analytical methods (PIXE, ESCA, DPC and TEM) was used for this study.

For each welding situation, welding parameters such as current and voltage have been varied. The choice of welding parameters affects mainly fume emission but also to some extent the elemental composition of the fume. For all the welding situations examined, the mass median aerodynamic diameter was less than 1 μm . This implies that most of the particles in the welding fume are respirable. No significant change of particle size was observed when the welding parameters were varied.

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ACKNOWLEDGEMENTS

I am deeply indebted to Roland Akselsson, my instructor and colleague, for his encouragement and stimulation throughout all the years. His deep knowledge and his scientific carefulness and guidance have been very important for the realization of this work.

I am also very grateful to Sven Johansson, one of the pioneers in this field, for his great interest in the development of the PIXE-method.

To all the present and former members of the PIXE-group (Mats Ahlberg, Mats Bohgard, Lars-Eric Carlsson, Hans-Christen Hansson, Eva-Marta Johansson, Katarina Johansson, Thomas B Johansson, Hans Lannefors, Li Hung-Kou and Jan Pallon), I wish to express my thanks for many stimulating and lively discussions of this work and other subjects.

The fruitful cooperation of Henry Kaufmann is gratefully acknowledged as is everything he has taught me about programming and about the HEX-program.

The help and support of the following individuals are highly appreciated and is acknowledged with gratitude:

- Knut Sjöberg, Preben Jensen, Erik Karlsson and Lars-Berne Nilsson for skilfully building and constructing the experimental set-up.
- Ragnar Hellborg, Kjell Håkansson and Christer Nilsson for an excellently well-maintained accelerator laboratory.
- Folke Brundin and Alex Simonsson, whose knowledge of welding has been extremely valuable in this work.
- Britt-Marie Kallerhed and Anna-Lena Johansson, the secretaries of the department, whose careful work and readiness to help at all time was much appreciated.

- Britt Hansson and Elna-Greta Broomé who were responsible for all the well-made illustrations of this work.
- Lisbeth Ottosson for artistic assistance.

I am very grateful to the staff of the PIXE-laboratory at the Niels Bohr Institute in Copenhagen, who placed their accelerator at our disposal at the beginning of this work and to the Swedish Work Environment Fund for the financial support which made the work possible.

I also want to thank my parents and friends for their support and stimulation.

Last, but not least, I want to thank Klas for everything.

A FACILITY FOR MULTIELEMENTAL ANALYSIS BY PIXE AND THE $^{19}\text{F}(\text{p}, \alpha\gamma)^{16}\text{O}$ REACTION

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Specific advantages with Particle Induced X-Ray Emission are: its 1) multielemental capability, especially when combined with nuclear techniques for lighter elements, 2) speed, 3) low detection limits for small samples and 4) accuracy. To make full use of these advantages, analytical parameters have to be chosen optimally and the facility to be carefully designed. This paper describes an experimental facility constructed to permit continuous development work to optimize the analytical conditions and to allow the gradual implementation of automatic control. Emphasis is also put on the simultaneous use of proton induced gamma rays from fluorine. The features and the performance of the set-up including its accuracy, precision and experimental detection limits are reported.

INTRODUCTION

Particle Induced X-Ray Emission, PIXE, has been a rapidly developing analytical technique over the last decade. Since 1970, when Johansson et al presented their pioneering paper,¹ PIXE has been applied in many different fields of science, e.g. atmospheric chemistry and medicine. Two International Conferences on Particle Induced X-Ray Emission and its Analytical Applications held at Lund in 1976 and 1980 have clearly demonstrated this development^{2,3}.

To make extensive use of the specific advantages of PIXE, e.g. multielemental capability, speed, low detection limits for small samples and accuracy, appropriate experimental arrangements and procedures have to be developed.

As compared to other X-ray techniques, one of the major advantages of PIXE is the possibility of simultaneously using the information carried by nuclear reaction products including the scattered projectile particles and hence extending its analytical capability also to elements lighter than sulphur. The feasibility of using Particle Elastic Scattering Analysis (PESA) has been shown

at several laboratories^{4,5}. Most PIXE-laboratories, however, use 2-4 MeV protons which limits the usefulness of PESA to the analysis of major (light) constituents and to the determination of total sample mass⁶. The gamma rays from nuclear reactions are the other possible source of information on light elements. The advantages of using such gamma rays have been demonstrated in several articles^{7,8}.

Due to its high abundance in some common welding rods, fluorine may be found in high concentrations in air in work places, being sometimes the first element to exceed its hygienic threshold limit value. Particular interest in the characterization of welding aerosols at our laboratory⁹ has initiated the development of a procedure for analysing fluorine using the $^{19}\text{F}(\text{p},\alpha\gamma)^{16}\text{O}$ reaction simultaneously with PIXE.

For studies of the fluorine depth distribution in various matrices the $^{19}\text{F}(\text{p},\alpha\gamma)^{16}\text{O}$ reaction has been used extensively, making use of the resonance character of the cross section^{10,11}. In order to obtain the total mass of fluorine in samples of thicknesses from 0.1 to 1 mg/cm², e.g. in an aerosol sample on a filter from a work place investigation, it is necessary to have a yield of gamma rays per fluorine atom which is almost independent of the depth in the sample. As will be further discussed, protons with energies of about 2.5 MeV, which fortunately is also an energy well suited for PIXE analysis, can be used for this kind of analysis.

The design of the experimental set-up is crucial for optimal use of the speed, the low detection limits and the accuracy of PIXE. To facilitate continuous optimization, the set-up is characterized by flexibility and prepared for automatic control. This has been achieved at the price of increased complexity which introduces some extra concern about charge integration.

In this paper, the system for PIXE and fluorine analysis and its performance are described.

THE PIXE FACILITY

Basic design

The vacuum chamber of this facility for combined X-ray and gamma ray analysis is

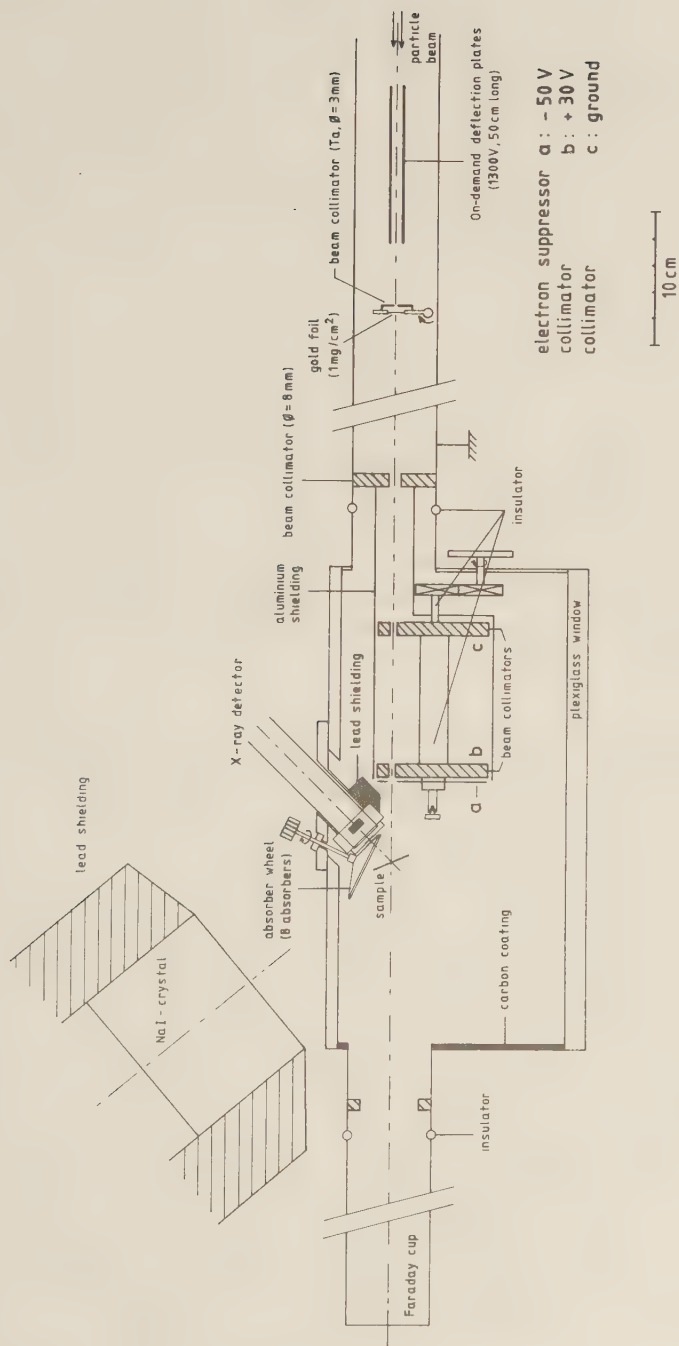


Fig. 1. Irradiation chamber for simultaneous X-ray and gamma ray analysis.

is shown in fig. 1. The size and shape of the chamber are partly determined by the demands for flexibility mentioned above. It is constructed from stainless steel and partly covered on the inside with carbon plates to reduce the characteristic X-ray background caused by scattered protons. On the top and the front walls exchangeable plexiglass windows allow observation of the interior parts. A "revolver" including ten sets of circular carbon collimators (table 1), each set consisting of a pair of collimators separated by 10 cm, allows the selection of a proper beam diameter from outside the chamber. The choice of beam diameter depends on the type of sample and the specific analytical task. Between the target and the last collimator a secondary electron suppressor ($U = -50$ V) is inserted to prevent the escape of electrons from the charge measurement region. The collimator revolver is shielded from the irradiation chamber by a grounded aluminium foil. In order to achieve a proton beam with a constant intensity distribution over its entire cross section, the beam is passed through a thin gold foil (1 mg/cm², gold evaporated on to glass plates and then floated off on water and fixed to a frame) situated 0.6 m before the target. This foil represents a compromise between having a homogeneous beam at the target and the consequent reduction in beam intensity (about a 15-fold reduction for 8 mm beam diameter). Since with this beam diameter it is anyhow possible to obtain a current of 200 nA at the target, this intensity reduction does not represent a severe limitation.

A Si(Li)-detector (Kevex, sensitive area: 80 mm², crystal thickness: 5 mm; resolution: 158 eV at 5.9 keV) is inserted into the chamber wall, at 135° relative to the beam (which gives a lower intensity of electron bremsstrahlung than at 90°, ref.¹²) with a distance of 0.040 m between the target and crystal. To maintain vacuum (better than 10⁻⁴ torr) but allow low energy X-rays to leave the chamber, a window (110 μm beryllium) is attached between the detector window (25 μm beryllium) and the target. The large variety of analytical situations places considerable demands on a proper choice of X-ray absorber and hence a wheel fitted with 8 different X-ray filters (see table 1) allows the insertion of an absorber suitable for the specific analytical situation. A stainless steel compartment beneath the chamber, designed for the 5x5 cm² standard photographic slide frames which are commonly used at many PIXE laboratories, contains a slide tray taking 40 samples. This compartment is evacuated before the valve, separating the container from the chamber, is opened, thus minimizing the time wasted due to pumping. By electro-pneumatic remote control, a sample is positioned in the proton beam and after analysis automatically replaced by using computer steering. The sample changing procedure can be checked over a closed-circuit television network.

Table 1

Beam collimators: diameters (mm) : 1, 3, 4, 5, 7, 8, 9, 10, 12

X-Ray absorbers:

<u>material</u>	<u>thickness (μm)</u>	<u>hole (%)</u>
Mylar	77	—
Mylar	340	—
Mylar	340	1.66
plexiglass	1110	—
aluminium	53	0.12
aluminium	152	—
aluminium	154	1.78
aluminium	310	(x)

(x) Double layer absorber made from two 155 μm aluminium foils, one with 4.3% and one with 0.06% relative hole areas. The foils are put together with coaxial holes. This absorber is specially designed for the analysis of geological material⁸.

Table 1. Diameters of the beam collimators and specifications of the X-ray absorbers which can be selected in the set-up discussed.

With a sample in position for analysis, the sample mounting frame (aluminium) automatically makes electrical contact with the chamber. This facilitates the charge transport, especially from thick samples, thus reducing the risk of charge build-up. However, for highly insulating thick samples, local positive voltages may reach several tens of kilovolts before electrical discharges occur and due to the acceleration of electrons towards the positively charged sample, a significantly increased electron bremsstrahlung background will occur in the X-ray spectrum. To avoid this, a battery operated carbon filament is used to spray the sample with electrons¹³. The use of a closed battery circuit prevents the introduction of false currents which might spoil the current integration. The latter is made using a current digitizer (ORTEC 439) and a scaler to count the number of charge pulses. For very low currents ($< 2 \text{ nA}$), special precautions are necessary so as not to disturb the current measurement. No one is allowed to move close to the set-up, since changes in the chamber capacitance may be

induced. Further careful grounding of surrounding equipments and electronics is required to reduce induction of currents.

X-rays produced in the sample by proton (2.55 MeV) bombardment are detected in the Si(Li) crystal producing signals which after passing a preamplifier enter an X-ray amplifier (Kevex 4525P) and a fast leading edge discriminating system (ORTEC 474 + ORTEC 406A). Pulses from this system trigger an on-demand beam deflection device¹⁴. About 400 ns after the detection of an X-ray event an electron tube (PL 519) grounds one of two parallel plates, normally kept at 1300 V and situated about 0.7 m up the beam line. The sudden electric field between the two plates deflects the proton beam from the target and keep it off while the X-ray amplifier is busy processing the X-ray event (for an 8 μ s amplifier time constant the processing time is approximately 80 μ s). Due to this on-demand beam system, radiation damage, sample heating and pulse pile-up are reduced and the electronic dead-time is insignificant. The system is routinely operated together with the electronic pulse pile-up rejector of the X-ray amplifier to reject any events arriving while the beam is off.

After shaping and stretching in the X-ray amplifier, the pulse is fed to an analog-to-digital converter and then stored in a computerized multichannel analyzer (Nuclear Data 6620). The spectrum evaluation is done with the HEX computer code¹⁵ comprising non-linear least squares fitting. To improve the accuracy and to allow for the use of high count rates (up to 5000 cps), the code has been implemented with corrections for Si-escape peaks and pile-up peaks¹⁶.

The system calibration for quantitative PIXE analysis¹⁷ is determined by the repeated irradiation of 45 homogeneous single element standard foils of accurately known elemental masses (the accuracy of individual foils is stated to be better than 5%, ref.¹⁸). Careful measurements or estimations of physical parameters, e.g. sample-to-detector distance, detector crystal dead-layer thickness etc., are used to attain an initial calibration. A calibration curve is fitted to the measured elemental yields with special attention to the physical interpretation and by comparing it with the estimated initial calibration. This procedure is then repeated iteratively.

To determine the accurate thicknesses of the X-ray absorbers, they are calibrated by analysing suitable homogeneous samples with and without the respective absorbers. For absorbers with hole (to transmit part of the low energy X-rays), the solid angle of the holes are determined by irradiation of a

low-Z element sample with and without the absorbers. The efficient beam area of each collimator is determined by analysing a spot-sample of accurately known elemental mass. For further details regarding the calibration procedure, refer to ref.¹⁷.

The requirements for high sample processing rates are taken care of by preparing the set-up for computer control. At present, sample changing is made automatically and both beam collimators and X-ray absorbers are designed for remote control via stepping motor drives.

Charge measurement

The number of protons incident on the target is integrated by use of a current digitizer and to check its accuracy, a high impedance ($R_i = 1000$ megaohms) voltmeter was used to measure the voltage over a 10 megaohms precision resistor (inaccuracy below 0.1%). For currents higher than 10 nA the inaccuracy of the digitizer is below 0.5 % and for currents between 1 and 10 nA below 1 %. Hence, even at low beam currents, the inaccuracy of the digitizer will be insignificant.

The current integrator is normally connected to the irradiation chamber as well as to the Faraday cup. Measurements show that for 2.55 MeV protons in this special set-up and for the total thickness of sample and substrate exceeding 3 mg/cm² it is necessary to collect the charge from the chamber as well as that from the Faraday cup. Unless this is done systematically a low charge will be measured, due to scattering of particles in the sample.

When striking the target, the protons will produce secondary electrons and some of those produced near to the surface of the material are emitted from the sample. The relative yield of such electrons will depend on proton energy and sample composition¹⁹. The total charge of these electrons has to be measured for accurate charge integration. To avoid the escape of the electrons through the last collimator, a negatively biased electron suppressor is inserted between it and the sample. In fig.2 the number of K X-rays per measured charge from an infinitely thick silver plate is plotted versus the negative bias of this suppressor. From the plot it can be inferred that at least -20 V is required in this special arrangement for accurate charge integration (the bias normally used is -50 V).

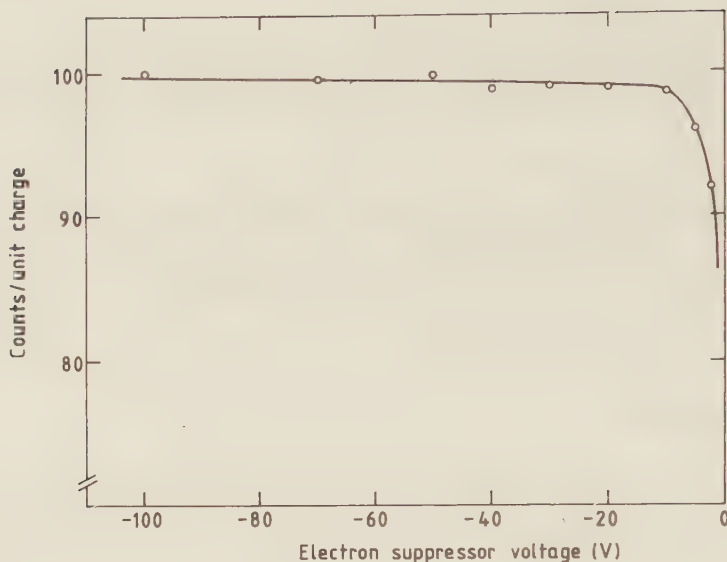


Fig. 2. Numbers of Ag K X-rays per measured charge (arbitrary units) from a thick silver plate plotted versus the negative bias on the electron suppressor. The proton current was 2 nA.

Due to the scattering of protons in the first collimator, some protons will hit the second collimator although this has a slightly larger diameter than the first one. To keep the secondary electrons produced in the last collimator from reaching the region of charge collection, it is kept at a positive voltage (+30V, empirically determined).

For accurate results the number of X-rays per unit charge should remain constant for different proton currents. To check for this, samples were analysed with varying currents and in fig.3 the number of Cu K X-rays per measured charge are plotted versus current for an infinitely-thick carbon pellet.

Since very low proton currents (1 to 5 nA) are occasionally used, the analysis will be very sensitive to erroneous extra currents. The on-demand beam system¹⁴ uses an electron tube for rapid grounding of one of the deflection plates. This system is a strong emitter of electromagnetic radiation, which may be picked up by parts of the current measurement system, thereby inducing extra currents in the nanoampere range. This can be checked with no beam on the target and an X-ray source on the detector to simulate normal count rates in the beam

deflection system. To avoid such currents, only coaxial cables are used and their shields are connected to ground at several points. There may also be other reasons for additional currents and this is an important problem worth much attention from any user of large irradiation chambers anxious to perform accurate ion beam analysis.

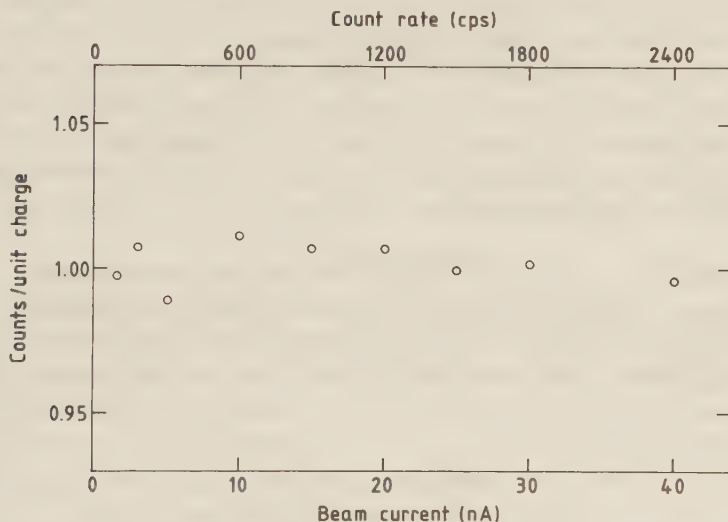


Fig. 3. Numbers of Cu K X-rays per unit charge (arbitrary units) versus proton beam current and count rate, when bombarding an infinitely thick carbon pellet. The statistical uncertainty in each determination is less than 1%.

Proton beam performance

The homogeneous current density over the beam cross section required for the analysis of small inhomogeneous samples is obtained by a diffuser foil. Such an arrangement causes a significant reduction in beam intensity as compared to the use of the electrostatic proton beam sweeping technique. The latter, however, has at least one significant disadvantage for the analysis of inhomogeneous samples: a well focussed beam of high intensity, swept at a kilohertz frequency over the sample, may induce a rather low average count rate, but can intermittently give rise to high rates. Since the probability for pulse pile-up

is proportional to the square of the instantaneous count rate, possible high local concentrations of elements present in an inhomogeneous sample will, in case of proton beam sweeping, cause enhanced pulse pile-up in the spectrum.

To check the beam homogeneity, the beam mapping method²⁰ has been applied. First, the beam is focussed and steered through the sample centre and then a diffuser foil (gold foil; 1 mg/cm^2) preceded by a small tantalum collimator (diameter: 3 mm) is inserted into the beam. To be able to reproduce its position, horizontal and vertical micrometer gauges are used. A small piece of copper foil was fixed to a polymer foil (Kapton, thickness $7.5 \mu\text{m}$) and moved horizontally and vertically stepwise in the plane of the sample through the beam with an 8 mm diameter. The number of X-rays (Cu K_α) was registered and normalized to the beam charge collected. In fig. 4a is shown the beam intensity distribution in the vertical direction.

For small samples, e.g. impactor samples, the measured numbers of X-rays will vary with their horizontal positions in the homogeneous beam because of the varying solid angle relative to the detector. In this case it is feasible to use a skew beam intensity profile with lower intensity at the side closer to the detector. In fig 4b. the horizontal beam intensity distribution has intentionally been made skew so that the measured number of X-rays is approximately constant. For comparison, the result of a beam scan with a homogeneous beam is also shown (broken line). This solid angle effect is still more pronounced when the X-ray detector is at right angles relative to the beam and with small distance between the sample and the detector. In these cases the solid angle changes relatively more with position for small samples. In the experimental set-up discussed here, a skew beam profile is used routinely.

The theory of multiple scattering by Meyer²¹ may be used for comparison with experiments and as a guide for designing a suitably-skew beam profile. Figure 4a shows very good agreement between theory and experiment.

The collimator pairs are made from carbon, the second one being somewhat larger than the first one so as to reduce the number of protons scattered out of the beam which would otherwise form a low intensity halo around the beam core. The use of the beam mapping method outside the beam core shows that, for a beam diameter of 8 mm, the current density of the halo 2 mm from the edge of the core is less than 0.1% of the core density. To reduce this further, the collimators are at present being replaced by tantalum collimators of anti-scatter design²².

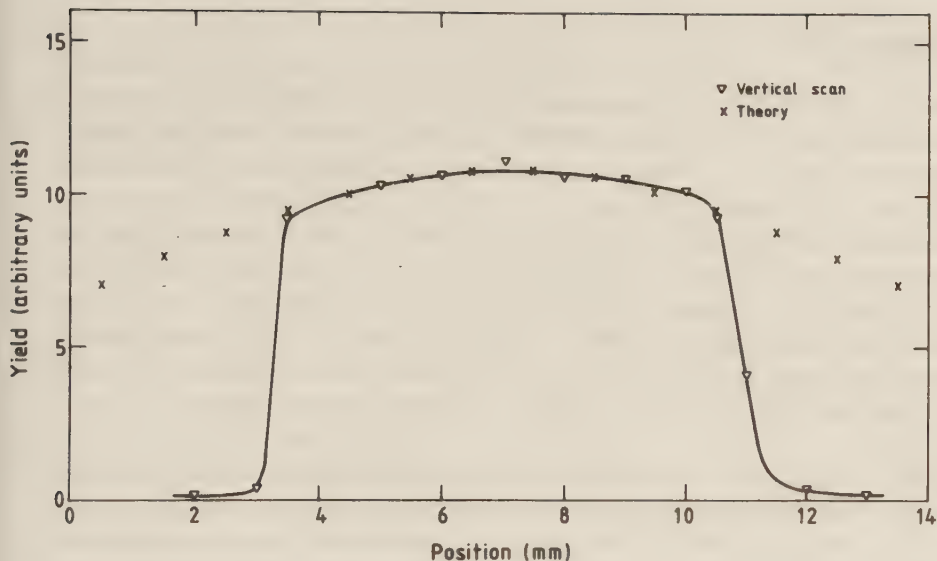


Fig. 4a. Experimental proton beam intensity profile in the horizontal (o) direction in the sample plane as measured by the beam mapping method²⁰. The beam collimator was 8 mm and the undiffused beam passed through the sample centre. For comparison, a theoretical profile based on the calculations by Meyer²¹ is also given (x).

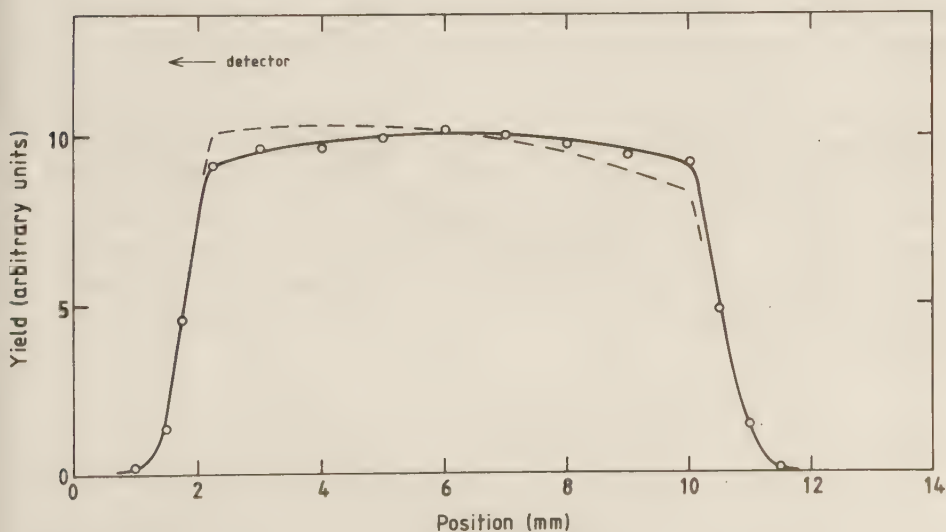


Fig. 4b. Horizontal beam scan for a skew beam intensity. The arrow points to the side closer to the detector. Small samples representing the same mass arbitrarily scattered over the beam cross section will in this case each yield approximately the same intensity. For comparison, a beam scan for a homogeneous beam is also given (broken line).

Detector effects

Particles scattered in the sample may, in cases when either none or a very thin X-ray absorber is used, reach the Si(Li) crystal with an energy of several hundreds of keV left. In such cases an event of very high energy is deposited in the detector. Frequent resets may occur in the optical feedback system of the preamplifier and severe distortions of the X-ray spectrum are obtained, e.g. peak broadening and peak centroid shift. Such effects render the X-ray spectra unsuitable for computer analysis and in severe cases may even render quantitative analysis impossible. This problem is avoided in the present set-up by using a beryllium foil of 110 μm thickness as window in the target chamber and thus still maintaining good transmission for low energy X-rays.

Similar distortions are also observed when bombarding certain kinds of targets, mainly those containing high concentrations of fluorine, e.g. aerosol filters made of Teflon fibres and some geological materials. The distortions are found even if a very thick absorber is used between the target and the detector. In these cases, high fluxes of gamma rays causes intermittent high (>1 MeV) energy depositions. This has been checked independently by analysing an X-ray spectrum and a gamma ray source (^{60}Co) simultaneously, obtaining the same kind of distortion of the X-ray peaks. Since the Si(Li) crystal cannot be shielded from gamma rays from the target position, samples producing an intense flux of high energy gamma rays have to be avoided. In some cases, it may be possible to select a proton energy having a low cross section for gamma ray production.

A significant background continuum in the X-ray spectrum is caused by gamma rays produced when the protons strike the collimators and then Compton scatter in the detector crystal²³. This yield is in particular significant when very thin targets with low intrinsic production of gamma rays are irradiated. By applying a lead shielding to the Si(Li) detector (see fig 1), the background for high X-ray energies is reduced by about 50% for 2.55 MeV protons and carbon collimators. By exchanging these for tantalum collimators, the background would be further reduced.

When X-rays are incident on the Si(Li) crystal close to the edge of the sensitive volume, incomplete charge collection may take place due to the distorted electric field pattern near the edge. As a result, the pulse height registered will be somewhat lower than the nominal pulse height from such an event. These degraded X-ray events form a low energy tail to the corresponding

full energy peak²⁴. This introduces difficulties in peak area determinations and an increased background for lower energy peaks riding on the tail. The effect can be reduced at the expense of reduced detector solid angle by inserting a collimator in front of the crystal and thereby preventing the X-rays from interacting in the poor electric field region.

The 80 mm² detector in this set-up is collimated to an approximate efficient sensitive area of 30 mm² by a tantalum collimator in front of the detector window. This reduces low energy tailing significantly as can be seen by comparing spectrum a and spectrum b in fig 5a. However, there is a significant residual tail which may cause slight problems in computer spectrum analysis. By bringing the detector bias to zero and then directly back again to its normal voltage (-1000 V) a significant decrease of peak tailing is achieved as can be seen in spectrum c in fig 5a. To check the time variation of the tailing after applying the detector bias, a ⁵⁵Fe-source was placed 10 mm in front of the detector (without collimation). The detector bias was applied and then pulse-height spectra were recorded after different times. In fig 5b the spectra are superposed, showing the gradual increase in peak tailing with time. When a

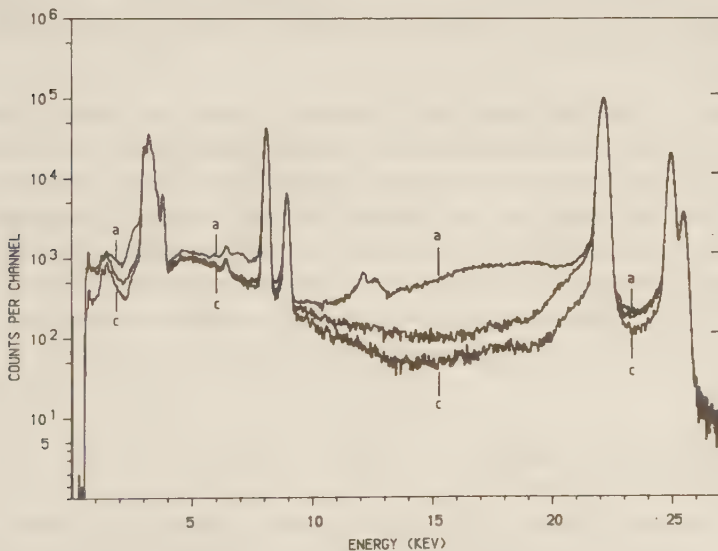


Fig. 5a. X-ray spectra from bombardments of a thick silver plate. The beam diameter was 8 mm and an external X-ray absorber of 340 μ m mylar was used. The total accumulated number of counts is the same in all three cases. In spectrum a, the whole Si(Li) crystal area (about 80 mm²) was exposed to the X-rays and in spectrum b, a tantalum collimator was placed outside the Be-window of the detector thus reducing the effective crystal area to 30 mm². In spectrum c, a temporary further reduction in low energy peak tailing was obtained by removing and immediately reapplying the detector bias.

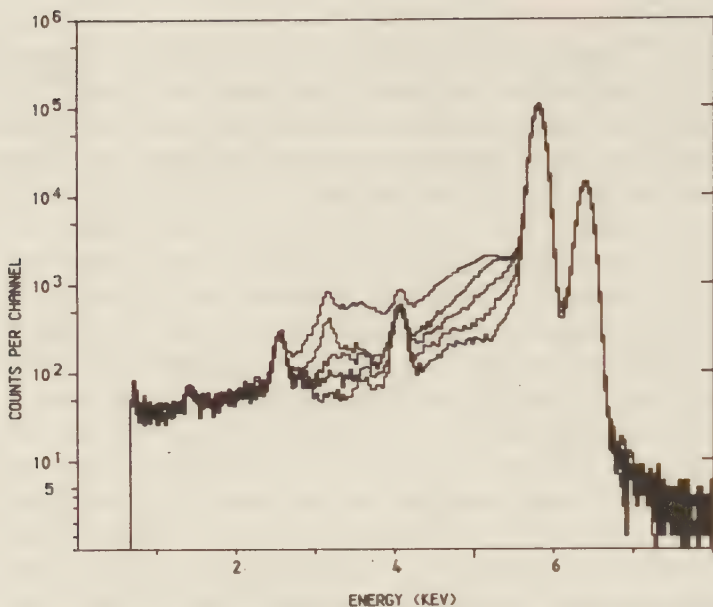


Fig. 5b. Pulse-height spectra from a ^{55}Fe source accumulated at different times after applying the detector bias. The Si(Li) detector was uncollimated and the total numbers of counts in the spectra are the same in all cases. The spectra refer (from bottom to top) to measurements at 0, 20, 60, 120 and 700 minutes after application of the bias.

small collimator is used and thus X-rays only are incident at a small central part ($\approx 10 \text{ mm}^2$) of the sensitive area of the detector, the peak tailing is as low as in case of a recently applied voltage. A tentative explanation for these effects is that, at least for the detector discussed, the on/off-procedure of the detector bias increases the charge collection efficiency in the poor electric field region at the crystal edge. Nothing has been found about this phenomenon in the X-ray detector literature and presumptive customers are advised to pay some attention to this effect when purchasing detectors.

Calibration and detection limits

In ref.¹⁷ the mass calibration of the PIXE system is described in detail. The accuracy in the determination of random elements is estimated to be better than 5% and is still better for ratios of elements. This accuracy refers to the routine analysis of an unknown thin sample.

To check the stability of this mass calibration, a quality control sample has

been run with each batch of samples (≤ 40 samples). By repeated analyses (800 times) of this sample over a year, the long term stability for homogeneous samples is shown to be better than 2.5% and for inhomogeneous samples better than 4% (one S.D.).

Detection limits for PIXE analysis are sensitive to the experimental conditions. To illustrate the capability in routine analysis of the PIXE arrangement described, interference-free mass detection limits were determined in the following way: A thin polystyrene foil (about $30 \mu\text{g}/\text{cm}^2$) was bombarded by a 150 nA proton beam with a diameter of 8 mm. The total accumulated charge was 40 μC . A 75 μm Mylar X-ray absorber was used. The detection limits were calculated as the mass corresponding to $3\sqrt{B}$ pulses, where B is the number of counts in the background within an interval of ± 2 S.D.s around the Gaussian peak (see fig 6).

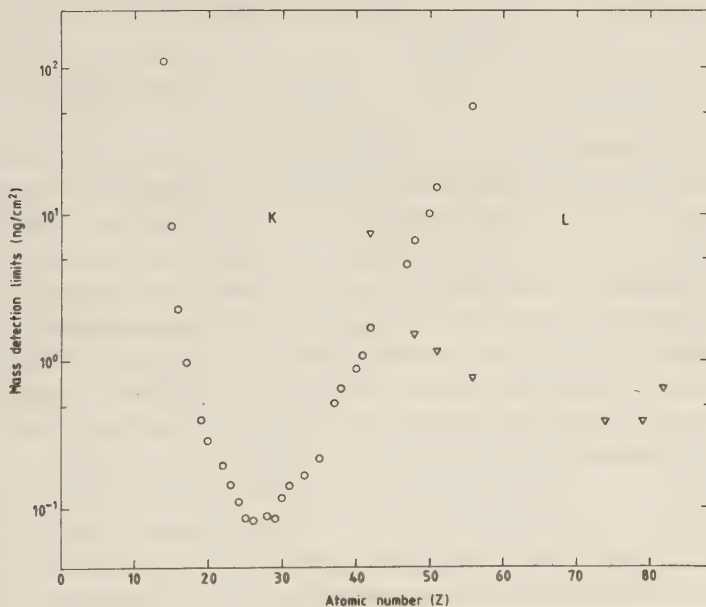


Fig. 6. Experimental mass detection limits versus atomic number calculated assuming no interference between adjacent lines. A 8 mm diameter beam was used to irradiate a thin (about $30 \mu\text{g}/\text{cm}^2$) polystyrene foil with few minor impurities. The total accumulated beam charge was 40 μC and an external X-ray absorber of 75 μm was used. The detection limits have been calculated as the mass which corresponds to $3\sqrt{B}$ pulses, where B is the background area below ± 2 S.D.s of the Gaussian X-ray peak in question. o and ∇ are determined for K- and L-lines respectively.

FLUORINE ANALYSIS

Physical principles and proton energy

When ^{19}F nuclei are bombarded with protons of MeV energies there is a high cross section for nuclear reactions forming $^{20}\text{Ne}^*$ -nuclei in excited states. The $^{20}\text{Ne}^*$ -nuclei de-excite by alpha particle emission to excited states in ^{16}O , which de-excite promptly to the ground level by the emission of gamma rays with energies 6.13, 6.92 and 7.12 MeV respectively²⁵. Due to the high energy of these gamma rays, they easily penetrate the walls of the irradiation chamber and can be detected by an external gamma ray detector.

The cross section of the $^{19}\text{F}(p,\alpha\gamma)^{16}\text{O}$ reaction as a function of proton energy E_p has a pronounced resonance character²⁶. Very sharp and high resonances for the production of the three gamma rays occur at $E_p = 0.873$ MeV, $E_p = 1.347$ MeV and $E_p = 1.374$ MeV. For E_p in the interval 2.0 to 2.6 MeV the sum of the intensities of these gamma rays (see fig. 7) shows a fairly smooth energy dependence remaining at a high value of cross section and, if the initial proton energy is selected to lie in the 2.0 to 2.6 MeV region and if the protons, after passing the sample, emerge with an energy above 2.0 MeV, the variation in gamma ray yield in the matrix will be less than $\pm 20\%$ (see fig 7). For the integrated matrix yield, the variation is still less and it is rather simple to correct for these small variations if the approximate sample thickness and composition are known. In the proton energy interval from 2.0 to 2.6 MeV the cross sections for proton induced gamma rays in other light nuclides are negligible compared to that in fluorine²⁷ and since the gamma lines (6.13, 6.92 and 7.12 MeV) are virtually free of interfering lines²⁷, the yields from possible competing reactions can be ignored.

Protons with energies of 2 to 3 MeV are the optimal projectiles for PIXE analysis^{28,29,30} and suitable sample thicknesses are up to 1 mg/cm^2 since such samples yield low background radiation and the results do not normally require corrections for particle slowing-down and X-ray absorption. Further, protons in the energy range 2.2 to 2.6 MeV are slowed down less than 0.2 MeV for these sample thicknesses and hence protons in this energy interval can advantageously be used for simultaneous PIXE and fluorine analysis.

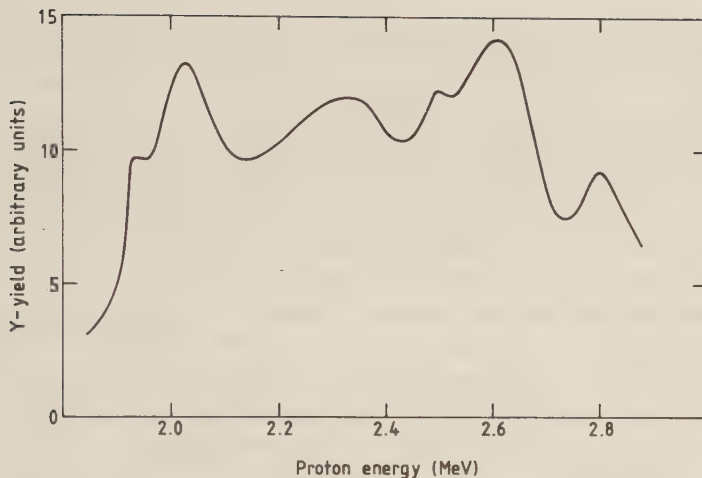


Fig. 7. Yield of high energy gamma rays from the reaction $^{19}\text{F}(p, \alpha\gamma)^{16}\text{O}$ in a thin target versus proton energy (after ref.^{2,6}).

Experimental arrangement

To match the low detection limits possible with PIXE, a large volume detector is preferred for the high energy gamma ray detection. Since no interference of any significance is expected, a large sodium iodide crystal is a good choice.

The practical detection limits are set by the background radiation. The material in collimators, chamber walls, etc., may contain substantial amounts of fluorine and will also be continuously contaminated with fluorine during the bombardment and handling. Since $^{19}\text{F}(p, \alpha\gamma)^{16}\text{O}$ reactions take place in the material of the experimental set-up with significant solid angle relative to the detector and since these high energy gamma rays have a high probability of penetrating material on their paths to the detector, their intensities will determine the practical lower limits of detection attainable in a specific analytical system.

Hence, careful design and choice of material is essential to keep the proton induced background radiation low. It is also essential to shield carefully the gamma ray detector from the natural background radiation emanating, e.g. from the concrete walls of the laboratory, since this could otherwise increase the detection limits.

In our set-up 2.55 MeV protons are used and the high energy gamma rays are detected in a 5x4" NaI crystal positioned at a distance of 0.15 m from the

target. Thick (0.06 m) lead shielding is incorporated around the cylindrical detector crystal (see fig 1).

For routine analysis, simple and convenient recording is obtained by a scaler with a lower level discriminator adjusted to count pulses referring to gamma rays produced in the $^{19}\text{F}(p,\alpha\gamma)^{16}\text{O}$ reaction only. The discriminator adjustment is carried out using a multi-channel analyser in the gating mode to set the discriminator level just below the double escape peak. The scaler is stopped after a preset accumulated beam charge. The number of counts normalized to the accumulated charge gives a relative yield, Y_s , for the known standard sample with a fluorine content C_s (mass per unit area). The blank substrate which is used to carry the fluorine standard is then irradiated giving another relative yield, Y_{sb} , which is subtracted from Y_s to get the net fluorine yield for the standard. To improve the accuracy of the calibration, several homogeneous standard samples with different fluorine compounds are normally analysed.

The unknown sample, containing the fluorine mass C_u per unit area, is then irradiated similarly to the standard foil, giving a net yield of Y_u . From an analysis of the substrate, Y_{ub} is obtained. Since different samples may be analysed for varying lengths of time and often significantly longer than the standard samples, the influence from natural background radiation should preferably be corrected for as well. This background component is dependent on the collection time and is essentially independent of the accumulated beam charge. Consequently all counts have to be reduced by t times Y_{bt} , where t is the real analysis time and Y_{bt} the number of background events per unit real time. The mass of fluorine per unit area can then be calculated from the following simple formula:

$$C_u = C_s \cdot (Y_u - Y_{ub}) / (Y_s - Y_{sb}),$$

where $C_s / (Y_s - Y_{sb})$ can be the average result from several standard samples. If very high count rates are used, significant electronic dead-time occurs and has to be corrected for.

In our set-up the beam passes through a diffuser foil to permit the analysis of heterogeneous samples. In this foil about 95% of the protons are scattered from their initial direction and out of the beam hitting tube walls and collimators, all of which are more or less contaminated by fluorine. A substantial number of gamma rays will thus be produced here and contribute considerably to the number

of fluorine counts. If, however, a well-focussed beam is used without any diffuser foil (as is possible for homogeneous samples) and deposited in a Faraday cup far away from or well shielded from the NaI crystal (see fig 1), the relative contribution of gamma rays due to scattered protons is significantly reduced. The absolute lower level of detection is then improved by more than one order of magnitude (for this particular experimental configuration).

Performance and Discussion

The samples most commonly analysed at our laboratory are aerosol samples between 0.1 and 1 mg/cm² in thickness. Assuming homogeneous samples it is possible from proton stopping power data³¹ and the yield curve in fig 7 to calculate the integrated relative fluorine gamma ray yield as a function of sample thickness. This function is slowly varying and also slightly smoothened by the energy straggling, which takes place when the protons pass through the matter. The integrated yield from a sample is rather insensitive to the sample composition. In fig 8 the integrated yield of gamma rays from the $^{19}\text{F}(\text{p},\alpha\gamma)^{16}\text{O}$ reaction, without any corrections for straggling, are plotted versus sample thickness for three different matrices for an initial proton energy of 2.55 MeV (corrections for straggling would change the yield less than $\pm 2\%$ over the energy and thickness intervals in question). For samples thinner than 3 mg/cm² a crude

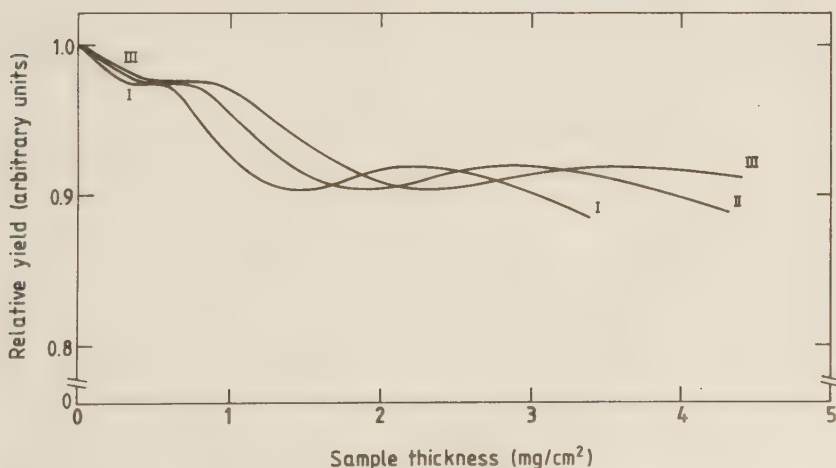


Fig. 8. Integrated relative yield of gamma rays from the $^{19}\text{F}(\text{p},\alpha\gamma)^{16}\text{O}$ reaction versus sample thicknesses for three different matrices: I) 100 % C, II) a welding aerosol matrix composed of 17% O, 20% F, 8% Si, 20% K, 10% Ca, 3% Mn and 22% Fe and III) 100 % Fe. An initial proton energy of 2.55 MeV and homogeneously distributed fluorine have been assumed.

estimation of the sample thickness (better than $\pm 20\%$) and of the sample composition facilitates a simple and accurate correction for sample thickness in fluorine analysis. The accuracy of the correction factor is estimated to be well within $\pm 5\%$. If the sample is not homogeneous, e.g. after sampling an aerosol with time-dependent composition, an estimation can be made from fig 7 to check for possible inaccuracies. Using a proton energy of 2.55 MeV and samples (welding aerosol matrix) thinner than 1 mg/cm^2 with all the fluorine in the first 0.1 mg/cm^2 or in the last 0.1 mg/cm^2 of the sample respectively gives errors of less than $+10\%$ and -10% respectively compared to the assumption of homogeneously distributed fluorine.

The dependence on thickness was checked experimentally by analysis of filters with different loadings of welding aerosols of constant composition. The samples were irradiated by 2.55 MeV protons and the yields normalized to the beam charge collected. In fig.9, the fluorine mass per unit area as determined by the procedure reported is plotted versus the aerosol sample thickness as determined gravimetrically. The circles represent values corrected for the sample thickness of the welding aerosol matrix (see fig 8). If no corrections at all are made, the maximum deviations from the solid straight line in fig 9 will still be less than 10% .

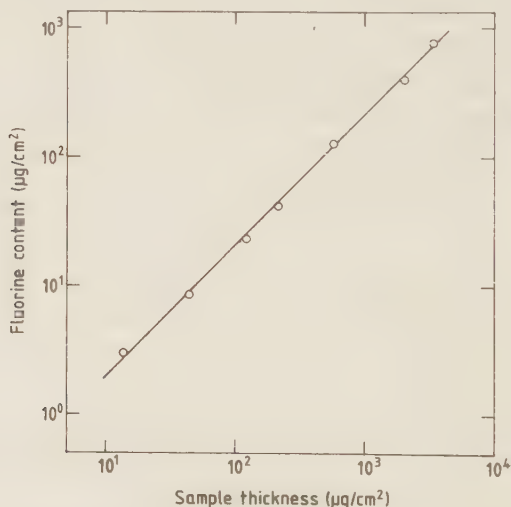


Fig. 9. Fluorine mass per unit area as determined by the $^{19}\text{F}(\text{p},\alpha)^{16}\text{O}$ method versus the gravimetrically determined sample mass density. Welding aerosol samples of different thicknesses but the same composition (identical to the one in fig 8 II) were used.

The lower limits of detection for analysis with the $^{19}\text{F}(\text{p},\alpha\gamma)^{16}\text{O}$ reaction depend on the probability of producing gamma rays, i.e. on initial proton energy and on sample thickness. Further system parameters, e.g. solid angle and efficiency are important. The detection limits will, however, also be depending partly on the intensity of gamma rays produced outside the sample and strongly on the proton beam characteristics and the surroundings of the beam.

If no diffuser foil is used and the beam is well-focussed so as not to hit the collimators, the absolute mass detection limit is at the same level as those of routine PIXE analyses for heavier elements. By irradiating known masses of a fluorine salt solution pipetted on to Nuclepore filters, the experimental detection limit has in this way been estimated to be 5 ± 3 ng fluorine within the beam area (about 2 mm^2). This rather low detection limit is only applicable to the analysis of homogeneous samples which do not require a homogeneous beam. The detection limit has been defined as the mass corresponding to 3 times the S.D. of the average yield from five blank Nuclepore samples.

For homogeneous beam irradiation, the detection limit is of course more dependent on the geometrical arrangement around the beam and on the shielding of the gamma ray detector. Sample carrying substrates, e.g. filters, vary considerably in thickness and hence the divergence due to multiple scattering when passing through the substrate varies with its thickness. Such scattering of the beam can have a slight influence on the level of background radiation. For routine analysis of samples collected on membrane filters (Nuclepore, thickness: 1 mg/cm^2), the detection limit in this particular set-up has been determined to $100\pm 25\text{ ng/cm}^2$. While being somewhat high compared to PIXE detection limits, this limit is quite sufficient for most applications. In welding aerosol samples, the fluorine mass per unit area is normally 10 to $200\text{ }\mu\text{g/cm}^2$.

The absolute analytical mass determinations are based on a comparison with homogeneous reference fluorine samples of known mass. The accuracy will then depend on the accuracy of the latter samples. The manufacturer states better than 5% accuracy¹⁸ for an individual foil and the accuracy may be further improved by the analysis of several different standard foils and using the average calibration value. In addition to this, errors are introduced because of inaccuracies in the charge integration when irradiating the sample and the standards and because of uncertainties in the corrections for proton slowing-down when the sample's thickness and composition are not accurately

known. The accuracy of the method has been checked experimentally by the analysis of known samples and by comparison with a standard procedure for fluorine analysis.

A very common analytical method for fluorine assaying, e.g. in welding aerosols, is to dissolve the sample followed by determination of the concentration of fluoride ions (F^-) in the solution with a fluoride ion selective electrode³². Only that part of fluorine which is soluble in the solvent used is analysed.

A comparison between the ion selective electrode and the $^{19}F(p,\alpha\gamma)^{16}O$ technique was performed with seven membrane filters, homogeneously loaded with welding aerosols of varying thickness. Each filter was cut in two equal parts, one of which was irradiated with protons and quantified according to the standard foil method described above. The welding aerosol on the second half was dissolved in 20 ml of distilled water and analysed with an ion selective electrode. For higher filter loadings, the solutions were diluted 10 to 25 times before analysis to avoid saturation of the electrode caused by excessive fluoride ion concentrations.

The seven filters (Millipore, diam: 37 mm, pore diam.: $0.8\mu m$) were loaded with amounts from 0.1 to 5 mg of welding aerosol (electrode ESAB OK 48.00) collected on to areas of about 8 cm^2 . A comparison of the results between the two methods of analysis gives an average ratio of $^{19}F(p,\alpha\gamma)^{16}O$ to ion selective electrode results of 1.05 ± 0.04 ($\pm$ one standard error of mean). This is close to unity and within the 5% accuracy for the reference samples stated above. However, the somewhat lower results for the ion selective analysis may be explained by incomplete dissolution of the fluorine from the welding aerosol due to the existence of a fraction of less soluble fluorine compounds. Most fluorine in the fumes from normal low hydrogen coated electrodes is water soluble due to the presence of alkali metals such as Na and K^{33} but sometimes the rather insoluble fluorine compound CaF_2 may also be present in the fume. The $^{19}F(p,\alpha\gamma)^{16}O$ method is not dependent on the chemical form of the fluorine and is further able to analyse nondestructively over a large mass interval. Hence it is very well suited for the analysis of aerosol samples in combination with PIXE analysis.

The precision of the method is mainly determined by the pulse statistics. For a homogeneous sample, the relative standard deviation attained with repeated analyses of the same samples was determined to be 1.5%. The uncertainties due to pulse statistics were less than 0.7%.

Simultaneous X-ray and gamma ray detection

The earlier mentioned possibility of a combination of PIXE and gamma ray detection for fluorine analysis is of great importance. This combination has been tested by irradiation of samples pipetted on to Nuclepore filters. A 1 g/litre stock solution of the salt K_2TiF_6 was used to prepare solutions of known concentrations. Using 5 μ l micro-pipettes, 5 to 20 μ l of the various solutions were pipetted on to filters thus obtaining spot samples with known elemental masses of F, K and Ti. The samples were analysed simultaneously for K and Ti by PIXE analysis and for fluorine according to the technique earlier described. In fig 10 the elemental masses determined are plotted versus masses calculated from known concentrations, volumes and the stoichiometry of the chemical compound. For samples well above the detection limits, the statistical uncertainties due to pulse counting were below 1%. Possible inaccuracies in the sample preparation procedure may account for part of the uncertainty.

The solid line represents the ideal slope 1.00. The correlations between the determined and calculated masses are excellent for all three elements ($r^2 > 0.9997$). For titanium and potassium, the slopes are 0.95 ± 0.01 and 1.02 ± 0.01 respectively and for fluorine 1.08 ± 0.02 (±one S.D.). From the error limits given, one can infer that only part of the deviations from the ideal line can be explained by the rather high uncertainties for low elemental masses close to the detection limits. The absence of experimental values for fluorine below 100 ng is due to the absolute mass detection limits being relatively higher than those of PIXE analyses. Although several sources of uncertainty are present, the good accuracy and agreement between the two methods show the analytical combination of PIXE and gamma ray counting for fluorine to be very versatile and powerful extending the analytical capability of the ion beam facility to an important element without increasing irradiation time.

In the section "Detector effects" above, it is shown that problems may occur when X-rays are detected in the Si(Li) crystal if simultaneously an intense flux of MeV gamma rays are incident on the crystal. Consequently, if a very large amount ($>1 \text{ mg/cm}^2$) of fluorine is present in the sample being analysed, it will be difficult to simultaneously perform PIXE analysis using the procedure described. For the sample thicknesses discussed above ($<1 \text{ mg/cm}^2$) and normal concentrations of fluorine from below 1% up to a few tens of per cent, this will not be a problem.

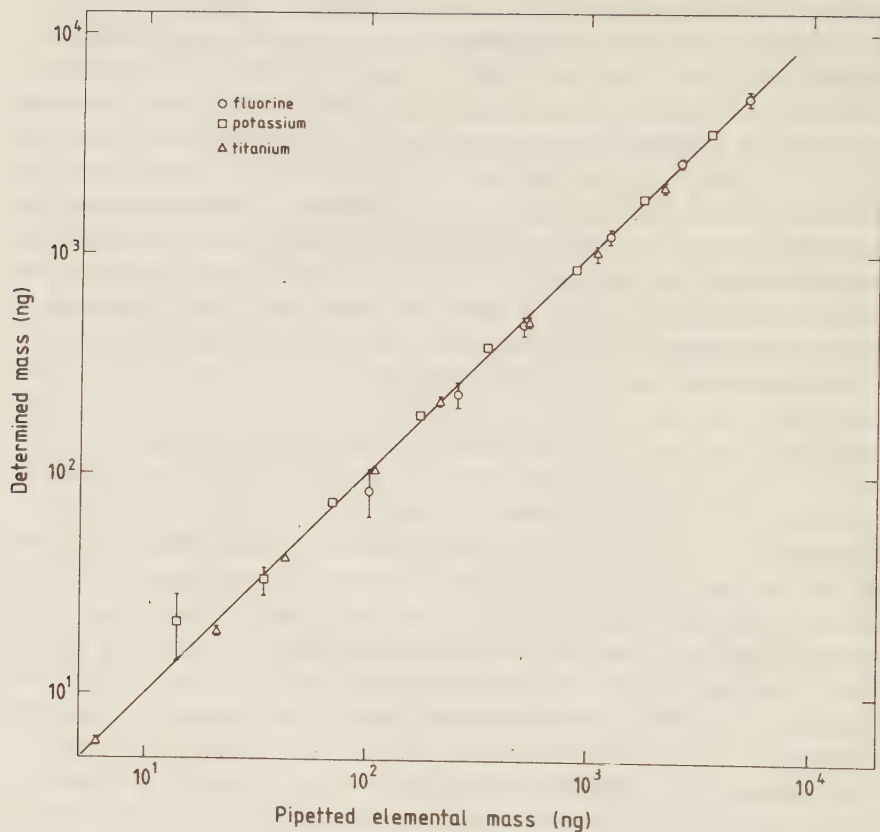


Fig. 10. Elemental masses of potassium and titanium as determined by PIXE and of fluorine as determined by simultaneous use of the $^{19}\text{F}(p,\alpha\gamma)^{16}\text{O}$ method versus the calculated masses of the respective elements. The data points refer to the averages of 5 determinations and the error bars represent one S.D..

CONCLUSIONS

The analytical arrangement developed constitutes an accurate and precise instrument for rapid multielemental analyses. Protons with energies of about 2.5 MeV, which in most applications give optimum general sensitivity for PIXE analysis, can be used for simultaneous and simple analysis of fluorine in thin samples ($<1 \text{ mg/cm}^2$) by detecting the high energy gamma rays from the reaction $^{19}\text{F}(p,\alpha\gamma)^{16}\text{O}$.

The irradiation chamber comprises an automatic sample changing system based on commercial slide frames, externally exchangeable X-ray absorbers and proton beam collimators, on-demand beam pulsing, beam diffuser foil and an electron emitting carbon filament for charge build-up reduction. Careful mass calibration and testing of the different components have been carried out and the set-up shows good overall performance and long term stability.

The impact of protons and intense fluxes of MeV gamma rays on the X-ray detector give distorted X-ray spectra. To avoid proton impact, a rather thick (110 μm) Be-foil is used as chamber window. To improve the X-ray spectra, the Si(Li) crystal has been collimated from 80 mm^2 to 30 mm^2 effective sensitive area thus reducing low energy peak tailing due to incomplete charge collection. Removing and reapplying the detector bias reduces low energy tails of X-ray peaks temporarily.

From comparisons with a standard method for fluorine analysis (ion selective electrode) and proton irradiation of samples with known masses of fluorine, potassium and titanium, it can be inferred that counting the gamma rays from the $^{19}\text{F}(p,\alpha\gamma)^{16}\text{O}$ reaction is an accurate and precise technique for fluorine analysis of thin samples, e.g. in aerosol samples, and that it can preferably be combined with simultaneous PIXE analysis.

ACKNOWLEDGEMENTS

The contributions of the following individuals to the work presented here is gratefully acknowledged:

R. Hellborg, K. Håkansson and C. Nilsson have been responsible for the excellently well-maintained accelerator laboratory at which this work has been carried out. The mechanical constructions were skilfully built by K. Sjöberg, P.

Jensen and L.-B. Nilsson and several of the electronic units were designed and built by E. Karlsson.

Finally, we are grateful to the members of the PIXE research group³⁴ in Lund for many stimulating and lively discussions and for valuable contributions to this work.

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CALIBRATION AND LONG-TERM STABILITY OF A PIXE SET-UP

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A general mass calibration procedure of a PIXE set-up is described. As an example, the results of the calibration of the PIXE set-up in Lund are given. For the calibration commercially available standards were used. The parameters of a physical model were adjusted to fit a calibration curve. To decrease errors due to inhomogeneities of the standard foils, the average from four different pieces of each foil was taken. The accuracy of the calibrated system in Lund is estimated to be better than 5% for individual elements and still less for ratios of adjacent elements.

For long-term quality control of the results, a special sample has been designed. This consists of a thick silver plate with a small copper spot in the centre. It is very sensitive to small changes in a PIXE set-up. By analysing this sample periodically, mistakes in the arrangement are promptly detected—a feature which is much appreciated in a mixed research, development and routine analysis laboratory. Also a measure of the long-term stability is obtained. For the Lund system, the long-term stability is 2.5% for a homogeneous sample and 4% for a small (inhomogeneous) sample.

1. Introduction

One important advantage of the PIXE-method compared to many analytical methods is the possibility of quantitative analysis without using standards. It is, however, initially necessary to establish a reliable calibration of the analytical system. This calibration may be performed in different ways. One approach is to procure accurate values of all the individual physical parameters of the system. Another way is to determine a sensitivity factor for each element of interest by fitting a calibration curve to experimental values. The second calibration procedure probably gives more accurate results than the first one if many good accurate standard foils are used. The second procedure is also less time-consuming.

In the Lund PIXE laboratory, we use mainly a calibration procedure suggested by Akselsson et al. [1]. In this procedure, we try to minimize the uncertainty of the calibration by using a physical model to guide the fitting procedure in the second method.

To maintain high analytical quality, it is important not only to have an initially accurate calibration but also to secure good stability of the experimental arrangement. This can be made by periodically analysing samples sensitive to any significant changes in the system.

2. The PIXE arrangement in Lund

Since the Lund PIXE set-up will be used as an example in the following discussions, a short description of the set-up will be given. For routine experiments, 2.55 MeV protons from a 3 MV Tandem accelerator (NEC 3 UDH) are used. For maximum flexibility in the set-up a large irradiation chamber was constructed (fig. 1). The chamber was used both for routine analysis and for developments of the PIXE-method. One disadvantage of a spacious chamber, however, is the more complicated charge integration required. In our system, we integrate the beam current both on the chamber itself and in a Faraday cup. To get an accurate charge integration, we use a secondary electron suppressor system, applying +30 V to the last collimator and –50 V to the electron shield between the sample and the last collimator (see fig. 1). For routine purposes, we recommend a smaller chamber.

A homogeneous beam is obtained by using a thin (~ 1 mg/cm²) gold-foil to diffuse the beam, and the beam-diameter may be varied from 1 mm to 1 cm by external collimator control.

The X-rays produced are detected in an 80 mm² (collimated to an effective area of 30 mm²) Si(Li) Kevex detector with an energy resolution of 158 eV at 5.9 keV. Instead of an ordinary pile-up rejector, we use an on-demand beam deflection system giving a pile-up interval of 300–400 ns.

A surface barrier ring detector to measure back-scattered particles and a NaI-crystal for gamma-ray detection are also included in the system (fig. 1).

To avoid charge build-up on thick insulating samples, a battery operated electron emitting carbon filament [2] is located close to the sample.

3. Calibration procedure

The possibility of access to a certain type of accelerator and also the kind of samples to be analysed determine the kind of charged particles selected for PIXE-analysis. In the PIXE set-up in Lund, we use mainly 2.55 MeV protons. The proton energy has been calibrated using the 1.374 MeV (p, γ)-resonance for fluorine, by irradiating a thin CaF_2 -target evaporated on to a thick tantalum plate. The accuracy of the energy calibration is better than 10 keV.

3.1. Irradiation chamber performance

Before performing a mass calibration, it is necessary to test the linearity of the X-ray yield as a function of the count rate as well as of the accumulated charge. Fig. 2 shows the results of two such linearity tests of our system. Sample I has been irradiated using a moderate current (0.1–25 nA) giving count rates between 20 and 6000 c/s. For sample II, lower count rates (200–1300 c/s) and higher beam currents (10–65 nA) were used. No significant variation in the yield is found when the current is varied. When the count rate is increased a slight decrease in the

yield seems to occur. The difference between the maximum and minimum values is, however, only about 3%. To reduce pile-up peaks which could interfere with characteristic peaks in the spectra, most samples are analysed with a count rate below 2000 c/s. The maximum value of the current selected depends on the heat resistance of the sample irradiated and on the volatility of possible elements in the sample.

3.2. Calibration of thin, homogeneous samples

For the mass calibration, thin homogeneous and commercially available standards can be used. For our set-up, standards from MicroMatter Co were used [3]. These consist of a thin layer of the element of interest evaporated on to a Nuclepore filter. According to the manufacturer the accuracy is better than 5%.

The standards were analysed using a 0.53 cm² beam area and no external absorber except for the chamber window (Be). The count rates were all below 2000 c/s to reduce pile-up peaks in the spectra and the time of analysis was chosen to give a statistical error well below 1%. Altogether 45 different standard foils have been analysed for their K-lines. The stan-

Table 1

A list of the standard foils supplied by MicroMatter Co during 1977–1979. The standard compound is evaporated onto a Nuclepore filter.

Compound	Year of purchase	Compound	Year of purchase
Al	1977	As	1977
SiO	1979	CsBr	1977
GaP	1978	CsBr	1979
CuS	1977	RbNO ₃	1979
CuS	1979	SrF ₂	1977
CuS	1979	Y	1979
NaCl	1979	Nb ₂ O ₃	1979
KCl	1978	MoO ₃	1977
CaF ₂	1979	Ag	1979
Ti	1979	Ag-Hg	1979
V	1977	Cd	1978
Cr	1979	Sn	1977
Mn	1977	Sb	1978
Mn	1979	BaF ₂	1977
Fe	1978	BaF ₂	1979
Co	1979	WO ₃	1977
Ni	1977	Au	1978
Zn	1979	Pb	1979
		ThF ₄	1977
		UF ₄	1979

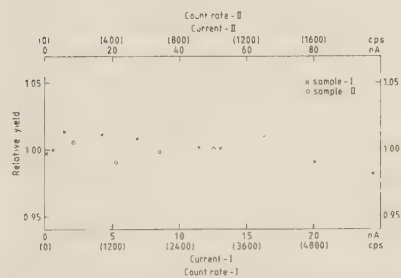


Fig. 2. Tests of the linearity of the X-ray yield (normalized to the mean) as a function of the beam current and the count rate for two different samples. The statistical error is less than 1%.

dards from the period 1977–1979 (see table 1) have been divided into four different pieces and all pieces have been analysed. The average value was used for the calibration.

A procedure often used in obtaining a calibration curve is to fit a nice-looking curve to the measured values and thus achieve sensitivity factors (counts/ $\mu\text{C}/\text{ng}$) for all elements [4]. We use a somewhat different approach in which the physical interpretation is stressed.

For our calibration, we use the formula:

$$A = c \cdot N / (P \cdot S \cdot T),$$

A = the mass per unit area of the element analysed (ng/cm^2),

c = a known constant ($0.00334 \times \text{atomic weight of the element}$),

N = the number of pulses in a peak per unit of charge [μC] $^{-1}$,

P = the X-ray production cross section in the peak (b),

S = the solid angle (sr),

T = the system efficiency.

To make a preliminary calibration, the X-ray production cross section is calculated from good results in the literature (e.g. from refs 5, 6 and 7). From simple measurements, the best possible estimates of the physical parameters of the analytical system (distance sample–detector, detector area, window thicknesses, thickness of gold and dead layer of the crystal, air gap and depth of the sensitive volume) are made.

Standards producing K-peaks of medium energy (4.5–17.5 keV) are used to determine the solid angle (S). The results for these elements are rather insensitive to small errors in the estimation of the system efficiency (T). We also check that the value of the solid angle determined is comparable within the uncertainties in the previous estimations of the distance detector–sample and of the area of the detector (total uncertainty <20%).

From results for lighter standard elements (1.5–4.5 keV), we determine the transmission through the system by making small changes of the used values of the window-thicknesses until we get by linear regression a horizontal line in fig. 3 in this energy region. By changing the value of the depth of the sensitive volume, the calibration for the heavier elements ($Z = 43$ –57) can be varied. Since the depth of the detector is about 5 mm, the system efficiency for the heavier elements is relatively independent of small variations in this value. A change in the depth of the sensitive

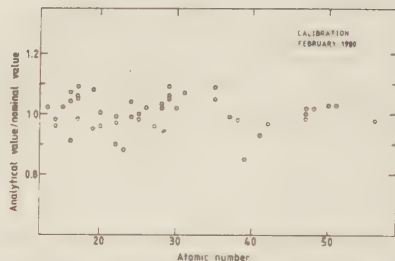


Fig. 3. The final results from the analyses of the standard foils divided by the values given by the manufacturer as a function of atomic number.

volume of the detector from 5 mm to 4.8 mm decreases the system efficiency by less than 1% for 30 keV X-rays.

Fig. 3 shows the results of the calibration after adjusting the physical parameters. The standard deviation of the mean is 0.8%. The following parameter values are used in our model: distance sample–detector 4.0 cm, detector area 0.28 cm^2 , chamber window $109 \mu\text{m}$ Be, air gap 0.4 cm, detector window $25.4 \mu\text{m}$ Be, gold layer $40 \mu\text{g}/\text{cm}^2$, dead layer $0.3 \mu\text{m}$ Si and depth of the detector 0.5 cm.

The manufacturer guarantees the stated thickness of each individual foil to be within 5% of its true value. The scatter of the results for adjacent elements as shown in fig. 3 indicates and further information from the manufacturer supports the supposition that any systematic component in the stated uncertainties is small. The error in the calibration due to uncertainties in the thicknesses of the standard foils is thus much smaller than 5%. Systematic errors in, e.g. cross section determination, charge integration and computer fitting of X-ray spectra all cancel out in the calibration procedure. If, however, any systematic errors occur only in part of the X-ray energy interval, they will remain. Such errors might be due to, e.g., local errors in cross section determination, incorrect estimation of the thickness of the detector gold layer or inhomogeneities in the detector crystal. The calibration curve in fig. 3 will give an estimate of the magnitude of this type of error. The accuracy of the calibration of a random element is estimated to be better than 5%. This estimation has been confirmed independently by Carlsson et al. [8], who used this calibration and thick target correction factors to obtain concentrations of several elements in some U.S. Geological Survey rock standards.

For heavier elements ($Z > 57$), the L-lines are used for mass calculation. To be able to calculate masses from different spectra containing L-lines using our fitting program [9], the relative intensities of the L-lines must be determined. This was performed by analysing thin single-element foils without any significant contaminations. By fitting the different peaks independently, their relative intensities can be determined.

The X-ray cross sections of the L-lines are not well-known and rather few elements have been analysed. Therefore a standard foil of each element of interest was analysed and the results used to determine a sensitivity factor for each element. The uncertainty of the calibration in this case depends directly on the accuracy of the single standard foil and due to outliers may exceed 5%.

3.3. Calibration of small thin samples

To carry out quantitative analyses using the PIXE method, it is necessary to have either a homogeneous sample or a homogeneous beam. When small samples (smaller than the beam area) are analysed, it is important to use a homogeneous beam. In our system the homogeneity of the beam is obtained by letting the beam pass a small collimator (3 mm diameter) followed by a thin gold foil (about 1 mg/cm^2). The distance between the diffuser and the sample is about 55 cm. To check the homogeneity of the beam profile, a small Ni-sample (diameter $\sim 0.3 \text{ mm}$) is scanned step-wise over the beam cross section [10].

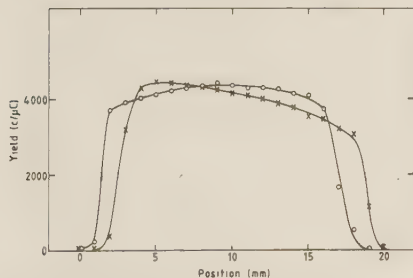


Fig. 4. The figure shows two vertical scans of the beam profile. A small (diameter $\sim 0.3 \text{ mm}$) Ni-sample has been used for the scans. In the first scan (o), the beam was on the cylinder axis of the accelerator tube (see fig. 1). In the second scan (x), the beam was about 3 mm off the axis.

Two vertical scans are shown in fig. 4. As can be seen from the figure, it is important that the undiffused beam hits the centre of the sample [11]. To guarantee this, the beam is collimated and steered so as to hit the sample centre. Without moving the beam, the gold foil is turned into the beam allowing the beam to pass the small collimator in front of it. The exact position of this collimator relative to the sample should then be maintained and is checked using micrometer gauges, horizontally and vertically. To attain increased homogeneity of the beam, it is possible to use a thicker gold foil or to increase the distance between the sample and the foil. Both these modifications will, however, decrease the beam intensity. The degree of beam homogeneity desired has to be weighed against beam intensity.

To be able to obtain quantitative results for a small sample from the mass calibration, the beam area has to be determined. By pipetting $5.00 \mu\text{l}$ of a standard solution (1.00 g of the element dissolved in 1.00 l of distilled water) on a Nuclepore filter, small and thin standard samples are prepared. The accuracy of an individual sample is better than 5%. From bombardment of these standard samples, the beam area for each collimator can be determined.

4. Homogeneity test of standard foils

The area of the standard foils used is about 11 cm^2 which should be compared with the area analysed (0.53 cm^2). If the standards are not homogeneous, this could introduce uncertainties into the calibration. When only a few standards are used for the calibration, this becomes especially important. All our standard foils, which were supplied by MicroMatter Co during the period 1977–1979 (see table 1), have been cut into four different pieces. All four pieces have one after the other been analysed with PIXE to check the homogeneity of the foils and, as mentioned above, to obtain a good estimate of their mean thicknesses. The beam current used when irradiating the standards has to be kept low to avoid losses of material or deterioration of the standard backing material. We normally used currents in the range $1\text{--}10 \text{ nA}$ and a beam area of 0.53 cm^2 . The maximum value of the proton current used on any standard foil was 20 nA . For the lighter elements (lighter than As), the irradiation time was typically around 100 s . An increase in the irradiation time was necessary for the heavier elements to get good statistics in

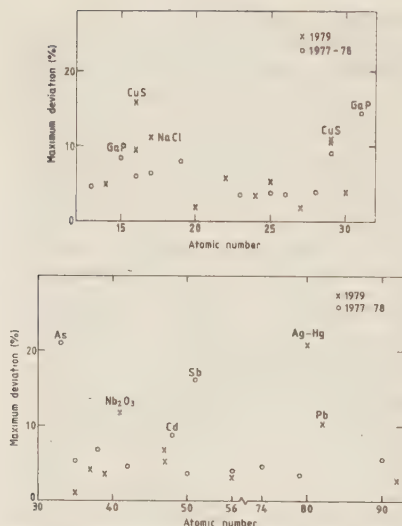


Fig. 5. The inhomogeneity of the different standard foils. The foils have been cut into four different pieces. In the figure is shown the maximum deviation (the maximum value minus the minimum value divided by the mean) in percent for different standards. For a single PIXE-analysis of a piece of a standard foil, the error due to statistics is less than 1%.

the peaks. When the same sample is analysed several times, the standard deviation is normally less than 1%.

In fig. 5 we have plotted the difference between the maximum and the minimum values of the separate pieces of a single standard foil as a percentage of the mean of all four pieces. For most of the foils, the deviation is in the range that might be expected but some outliers with a deviation of about 10% or more are present. The standard foils showing the largest deviations among their different pieces are GaP, CuS, NaCl, As, Nb₂O₃, Cd, Sb, Ag-Hg and Pb.

Using evaporation techniques when manufacturing standard foils may sometimes introduce a significant difference in thickness between non-adjacent areas of the foils. Since the thickness given by the manufacturer is an average value for the whole foil, our procedure of averaging the values obtained from the centre of each quarter of the foil is quite reliable. This statement is supported by the good agreement between the calibration values obtained in this way

(except for arsenic) from the less homogeneous standard foils and the values obtained from homogeneous standards of neighbouring elements.

However, there is another pitfall—the risk of losses of material due to the analysing technique used. Some of the parts of the standard foils used had been bombarded prior to this investigation which further accentuated this risk in our case. Repeated bombardments of foils revealed marked losses of arsenic and mercury (the silver of the Ag-Hg foil is not affected) in our experimental conditions. The extreme values for arsenic and mercury in fig. 5 may thus be explained by losses. The inhomogeneities of the NaCl, Nb₂O₃ and Pb foils are probably not accounted for by losses of material since the pieces of each foil which were earlier irradiated gave the highest values. The arsenic value was excluded from the calibration curve in fig. 3.

In other circumstances, the risk of loss of some elements other than As and Hg may constitute a problem, e.g., in calibration procedures using more damaging beams or using fewer different kinds of foils. Further investigations of losses from standards are currently in progress.

5. Quality control and long-term stability

It is very important for the users of all analytical methods to maintain good analytical quality. A well-calibrated system is not sufficient to guarantee this. Frequent checks of the stability and accuracy of the system must also be performed, e.g., by periodically analysing suitable samples.

For this purpose, a sample (or samples) which is quickly analysed and sensitive to significant changes of the analytical system should be used. It is also very important that simple errors due to operator oversight are rapidly detected. It is also important that the sample withstands all kinds of treatment without deteriorating, in order to make it possible to analyse the same sample over a long period of time. In our laboratory, MicroMatter standards (CuS) were originally used for quality control. We soon discovered that the standard backing material (Nuclepore) became fragile when irradiated for a period of time and that the standards were then easily damaged during handling.

The standard sample we have used for the last two years is made from a thick (1 mm) silver plate with a small piece (diameter ~1 mm) of copper foil in its centre. When analysing it, a beam current of 2 nA (count rate 2000 c/s) and a beam area of about 0.5

Table 2

The table shows probable explanations for different changes in the results from the analysis of the Ag/Cu-standard.

	Reason
<i>All peaks changed:</i>	Inaccurate charge integration. Detector badly positioned. Beam deflection system not working. Wrong secondary electron suppressor voltage.
<i>One peak changed:</i>	
Ag-L	X-ray transmission changed. Wrong angle between the sample and the detector.
Cu-K	Inhomogeneous beam. Collimator diameter not correct.
Ag-K	Wrong proton energy. Detector not working properly.

cm² are used and a 340 μ m Mylar foil is placed between the sample and the detector. To get a small statistical uncertainty (<1%) in the peaks of the spectrum, an irradiation time of 1 min is sufficient. The silver standard is analysed routinely before and after every batch of 40 samples and has so far been analysed more than 800 times.

In the spectrum from this Ag/Cu-standard, there are low energy peaks (Ag-L), medium energy peaks (Cu-K) and high energy peaks (Ag-K). In table 2, different patterns of changes in the areas of the peaks and their possible explanation are listed. When all peaks are changed by the same factor, it is often due to some error in the current integration. This error could be caused, e.g., by a leak current to or from the sample chamber or by not applying the correct voltage to the electron suppressors. Since a low current (2 nA) is used for the analysis of the sample, small variations in the charge integration can easily be detected. If the beam deflection system is not working, this gives a decrease of about 10% in all the peaks. Another reason for this kind of shift is a change in the solid angle, e.g., due to an incorrectly positioned detector.

When a variation mainly in the Ag-L peaks is detected, this is probably due to a change in the transmission of the X-rays. This kind of variation may also be due to a small change of the angle between the sample and the detector. A change of 5° from the normal angle of 22.5° gives a 7% error in the Ag-L peaks. The variation of the Ag-K peaks is then less than 1%.

If we find a change only of the Cu-K peaks, this is

probably due to beam inhomogeneity or because the beam area has been changed, e.g., by using the wrong collimator.

Finally, if the Ag-K peaks vary more than the other peaks, the reason may be that the proton energy is not correct. A proton energy of 2.65 MeV instead of 2.55 MeV gives an increased value for the Ag-K peaks of about 7%. Another explanation for the variation may be that the X-ray detector is not working properly.

We have also studied the long-term stability of our analytical system. The silver value (homogeneous sample) has a stability of 2.5% (= 1 standard deviation) over a one year period. The variation of the copper value for the same period was 4%. The larger variation for a small sample (spot) could be explained by changes in the homogeneity of the beam, as discussed earlier.

The variation over a long period should be compared with the variation when the sample is analysed several times during a short period (<3 h). The latter variation is less than 1%.

6. Conclusions

In the mass calibration procedure described, a fitting technique based on a suitable physical model is used. Another technique often used for calibration is direct fitting of a calibration curve to the measured values. One important advantage in using any fitting procedure is that single outliers of the results from the standard foils will have less impact on the calibration. Reasons for such outliers may be mistakes introduced during production or analysis of the standard foil, inhomogeneities of the foil or losses of standard material in the beam.

By using a physical model to guide the fitting procedure, errors due to incorrect standards in some part of the X-ray energy region can be further decreased. Especially when few standards are used, the direct fitting technique is very sensitive to the quality of the standard foils, and single outliers may introduce significant errors in the calibration. After having applied the calibration procedure described to our set-up, we estimate that an individual element can be analysed with an accuracy of better than 5% for elements with atomic numbers between 13 and 57 detected by their K-X-rays.

If only part of the available standard is analysed and rather few standards are used for the calibration, an additional error may be introduced due to inho-

mogeneities in the standards.

To maintain high quality in the analytical results, frequent controls of the calibration have to be made. A very versatile method for these tests of the stability, is the use of a thick silver plate with a copper spot. This sample is very sensitive to small changes in the analytical arrangement and withstands normal treatment without any noticeable deterioration. The long-term stability of the PIXE system in Lund is 2.5% for homogeneous samples and 4% for inhomogeneous. The short-term stability (<3 h) is better than 1%.

The authors are very grateful to the staff of the Pelletron laboratory in the Lund Institute of Technology for the superbly-equipped and maintained accelerator.

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ELIMINATION OF CHARGING IN THE PROTON-INDUCED X-RAY EMISSION ANALYSIS OF INSULATING SAMPLES

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Received 31 October 1975

Anomalous background due to charging in the proton-induced X-ray analysis of insulators is eliminated by inserting a heated carbon filament or by raising the pressure in the sample chamber.

Proton-Induced X-ray Emission (PIXE) has been shown to be a feasible analysing method especially for thin samples^{1,2}). The high sensitivity obtained is partly due to the lower level of the continuous background radiation found in proton bombardment compared with that arising when electrons or photons are used for excitation³⁻⁵). However, when the method is extended to the analysis of samples so thick that they stop the protons, the continuous background radiation is found to increase considerably when the samples are good insulators^{1,5-9}). We have also seen such an effect in thick filters when the protons can pass through. The samples become charged by the proton beam, and, in the discharge, electrons are accelerated producing an intense background of bremsstrahlung which may reach several tens of keV. This bremsstrahlung reduces the sensitivity due both to the higher background level and to the fact that the proton current has to be decreased to adjust for the higher count rate in the detector.

This Letter describes two ways of neutralizing the charge build-up: by inserting a hot filament emitting electrons a short distance in front of the target, as proposed by Shabason et al.⁹), and by increasing the pressure in the target chamber. Both methods avoid the danger of contamination associated with the evaporation of conducting materials on to the sample^{5,7}), or the mixing of target and conducting materials¹⁰).

The filament in the "electron-gun" presented in fig. 1 is taken from a commercial carbon filament bulb. Tungsten filaments were tried but found to contaminate the sample severely when heated. The carbon filament is clamped to two carbon rods. These are fastened to a cylinder of plexiglass so that no heavy elements are heated when the glow current is turned on. A voltage of 7 V, which gave a glow current of 0.25 mA, was sufficient to neutralize the charge from a 50 nA beam of 2 MeV protons. To prevent positive impurity ions

from the carbon filament contaminating the samples, a perforated cap of aluminum kept at +100 V was placed over the filament. The electron-gun was placed in front of the target in an insulated target chamber similar to that described in ref. 11, the batteries being placed outside the chamber at atmospheric pressure. The electric connections were made as shown in fig. 1. The proton current could then be integrated for quantitative determinations without any interference.

Another, simpler, way of neutralizing the charge build-up on thick insulating samples was found to be by increasing the pressure in the target chamber. In

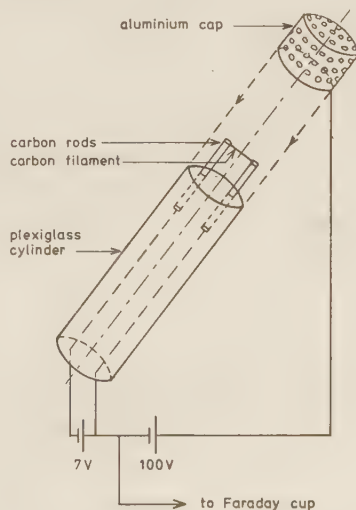


Fig. 1. The electron-gun used to spray the sample with electrons.

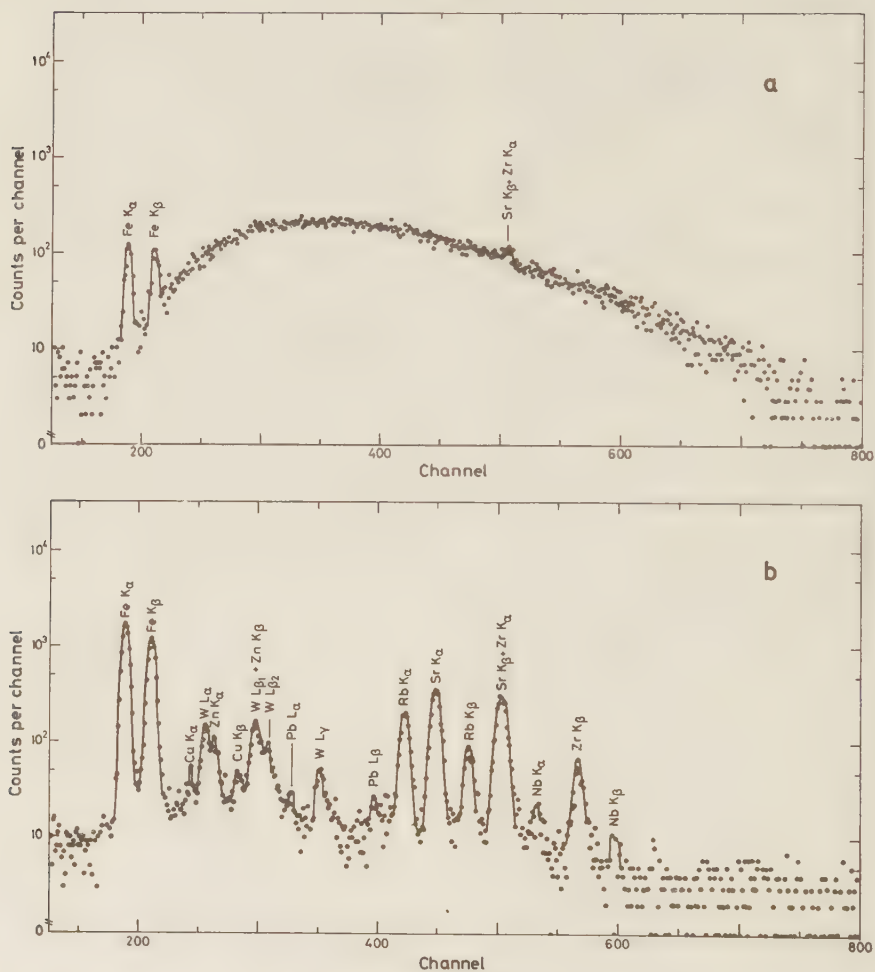


Fig. 2. The spectra from a 3 min analysis of a granite sample with 2 MeV protons, when the low energy X-rays are absorbed in a 280 μm thick aluminum absorber; (a) when charging limited the proton beam to 3 nA, (b) with a beam current of 50 nA, charging being eliminated by the use of a heated carbon filament in the sample chamber.

ELIMINATION OF CHARGING

the case of 2 MeV protons, the charging ceased when the pressure was raised to at least 1.5 Pa ($\approx 10 \mu\text{m}$). As the X-ray production cross section is a smooth function of proton energy, the slowing down of the protons due to the residual gas in the target chamber and by the very thin carbon layer which grows on the target at low pressure, do not affect quantitative determinations. However, as the residual gas in the target chamber may be a source of impurities, the electron-gun method is to be preferred, when possible.

The drastic decrease in sensitivity due to charging is illustrated in the two spectra shown in fig. 2. Both show a 3 min analysis of a powdered granite sample pressed to a pellet. When the spectrum in fig. 2a was recorded, charging limited the beam current to 3 nA which gave a count rate in the detector varying from 50 to 1000 counts per second. When the electron-gun was turned on, the charging was eliminated and a beam current of 50 nA gave a steady count rate of 400 counts per second, resulting in the spectrum in fig. 2b. The spectrum obtained without the electron-gun but with the pressure in the target chamber raised to 3 Pa ($\approx 20 \mu\text{m}$) was identical with that shown in fig. 2b.

The peaks correspond to 0.9% Fe, 5 ppm Cu, 20 ppm Zn, 40 ppm Rb, 70 ppm Sr, 60 ppm Zr, 5 ppm Nb, 100 ppm W and 5 ppm Pb. When calculating the concentrations, the attenuation of the X-rays and the decrease in X-ray production cross section due to the slowing down of the protons in the sample have been taken into account¹¹).

We have benefitted from discussions with Dr R. Akselsson and Dr T. B. Johansson. We are grateful to Mr K. Sjöberg for building the electron-gun, to Dr Z. Solyom, Dept. of Mineralogy and Petrology, University of Lund, for providing the granite sample and to the Van de Graaff laboratory at the Niels Bohr Institute, Copenhagen, for the possibility of performing this experiment.

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MODIFICATIONS OF THE HEX PROGRAM FOR FAST AUTOMATIC RESOLUTION OF PIXE-SPECTRA

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ABSTRACT

The computer code HEX for resolving PIXE-spectra has been modified. By irradiating standard foils, the escape ratios for X-ray peaks in the energy interval 3.3-10.6 keV have been measured. The results have been compared with theoretical calculations and experimental results of other research groups. The escape peaks have been included in the computer code. Pile-up peaks in the X-ray spectrum are also fitted by the modified computer program. This procedure is independent of the count rate and the pile-up interval. In addition an effective routine for dropping small X-ray peaks has been developed.

INTRODUCTION

A fast reliable computer program is essential for the full use of PIXE-analysis. One approach, the computer program HEX (earlier called REX), was explored by H.C. Kaufmann et al.^{1, 2, 3}. The development of HEX permitted good progress to be made in routine fast resolution of PIXE-spectra especially these from thin samples of ambient aerosols. The use of PIXE-analysis has however expanded, thus increasing and changing the requirements on the computer program for spectrum resolution. The analysis of different kinds of samples containing many elements places great demands upon the ability to resolve peaks. To avoid erroneous results, it is essential that the escape peaks are included in the computer code. To limit computer time, it is necessary to develop routines for dropping undesirable peaks and elements when analysing unknown samples.

One of the advantages of PIXE is its short analysis time. Its speed can be further increased by increasing the count rate, at the expense of larger pile-up peaks which must be handled by the computer program.

A version of HEX (HEX78) has been modified in response to the requirements described resulting in a new version HEXLUND81.

THE COMPUTER PROGRAM HEX

The computer program HEX is based on a physical model describing an X-ray spectrum as Gaussian distribution peaks on a continuum. The model uses experimental information from the literature, e.g., the relative intensities and energies of X-ray peaks, so as to increase the speed of spectrum resolution. By using a least squares algorithm similar to that suggested by Marquardt⁴, the linear and non-linear parameters of the model are fitted. The whole spectrum is fitted simultaneously thus avoiding discontinuities in the fit of the continuum.

Energy calibration	$E = P_1 + P_2 \cdot Z$
Resolution of the detector	$FWHM = \sqrt{P_3^2 + P_4^2 \cdot E}$
Continuum	$CONT = CONT1 + CONT2$
$CONT1 = T \cdot \exp(-P_2 C_1 Z) (P_6 Z + P_7 Z^2 + P_8 Z^3 + P_9 Z^4)$	
$CONT2 = P_{10}/E + P_{11} + T \cdot (P_{12} + P_{13} Z + P_{14} Z^2 + P_{15} Z^3)$	

Z = channel number I minus a fixed reference channel

E = X-ray energy

$FWHM$ = full width at half maximum

T = transmission through the system

C_1 = a constant

P_i = parameters

Table 1. List of the functions in the HEX78 version of the program for energy calibration, detector resolution and the continuum.

The version HEX78 contains five non-linear parameters, four of which describe the calibration and resolution of the peaks (see Table 1). The fifth non-linear parameter P_5 is the area of the sample analysed and is fitted when analysing spot samples of unknown area to facilitate a correct self-absorption correction. The background function retains ten linear parameters (see Table 1) and thirty-five other linear parameters are reserved for the elements fitted. The increase in background for all energies lower than the peak energy due to low energy tailing is partly taken care of by including a step function in the model. The low energy tail close to the peak is, however, not included in the model.

Before starting the fitting, an element library is read from a data file. This library contains data about the mass absorption coefficients and about X-ray peaks of each element. For a particular X-ray peak, its energy and relative intensity compared to other peaks of the same element are included. Information about the elements to be requested in the spectrum, starting values of the non-linear parameters and the experimental conditions (e.g., absorber and beam area) are also given.

HEX78 fits first the linear parameters using the fixed starting values of the non-linear parameters (P_1 - P_5). This is followed by a number of fits of both linear and non-linear parameters. This fitting procedure is interrupted when one of the following conditions is satisfied: the reduced χ^2 , the absolute value of each component of the vector $\nabla\chi^2$ or the relative change of all the parameters is less than preset values or if a maximum number of iterations has been performed. Finally, another fit of the linear parameters is made.

ESCAPE PEAKS

When an incident X-ray of energy E creates a vacancy in the K-shell of a silicon atom in a Si(Li) detector, either an Auger electron or a Si K X-ray (energy E_{Si}) is emitted. If the Si X-ray escapes from the sensitive volume of the crystal, an energy $E-E_{Si}$ is registered. This phenomenon creates a peak in the X-ray spectrum with an energy $E-1.739$ keV ($E_{Si\ K\alpha} = 1.739$ keV) and with the same full width at half maximum (FWHM) as an ordinary X-ray peak at energy $E-E_{Si}$. Since the escape peak and parent peak are created by the same X-rays, the ratio between the area of the escape peak and its parent peak is independent of absorption effects. The intensity of Si K_β is only 0.0294^5 of that of Si K_α and the energy of Si K_β is

1.836 keV and thus the escape peak from Si K_β is included in the Si K_α escape peak. If the detector is well-collimated and the detector crystal sufficiently deep, losses only occur through the front surface of the crystal.

Theoretical calculations

Assuming an infinitely deep and infinitely wide detector and X-rays incident perpendicular to the surface of the detector, the following formula can be derived for the fraction ϵ of the emitted Si K radiation which escapes from the detector^{6,7}:

$$\epsilon = 1/2 \cdot (1 - \mu_{\text{Si}}/\mu_i \cdot \ln(1 + \mu_i/\mu_{\text{Si}})) \quad (1)$$

Here μ_i is the photoelectric mass absorption coefficient in Si for the incident radiation and μ_{Si} the photoelectric mass absorption coefficient in Si for Si K radiation.

The escape ratio η (the number of counts in the escape peak/total number of counts in the escape peak and the full energy peak) is then equal to

$$\eta = \omega_K \cdot (r-1)/r \cdot \epsilon$$

where ω_K is the K shell fluorescence yield of Si and r the K absorption edge jump ratio.

The intensity (κ) of the escape peak to the parent peak is $\kappa = \eta/(1-\eta)$.

If the X-rays are not incident perpendicular to the surface of the detector, formula (1) is changed to⁸

$$\epsilon = 1/2 \cdot (1 - \mu_{\text{Si}} \cdot \cos\theta/\mu_i \cdot \ln(1 + \mu_i/(\mu_{\text{Si}} \cdot \cos\theta))) \quad (2)$$

where θ is the angle between the incident X-rays and the normal to the front surface of the detector.

In calculating theoretical values of the escape ratios, mass absorption coefficients from Veigele⁹ are used. The value of ω_k used is 0.0482^{10} and of $(r-1)/r$, 0.918^9 . In Table 2 are shown the calculated values of the escape ratios assuming perpendicular incidence of the X-rays. The theoretical calculations are affected by the uncertainty of the fluorescence yield value ($\omega_k = 0.0482 \pm 0.0041$) and the uncertainties of the photoelectric cross sections (2-5%). At higher X-ray energies, the neglect of multiple scattering in the physical model can give deviations.

Energy (keV)	Escape ratio (η)		$\eta_{\text{theor}}/\eta_{\text{exp}}$
	Theory	Experiment	
4	$0.00791 \pm 10\%$	$0.00816 \pm 2\%$	0.969
5	$0.00527 \pm 11\%$	$0.00544 \pm 1\%$	0.969
6	$0.00355 \pm 12\%$	$0.00374 \pm 1\%$	0.949
8	$0.00174 \pm 12\%$	$0.00187 \pm 2\%$	0.930
10	$0.00094 \pm 13\%$	$0.00104 \pm 5\%$	0.904

Table 2. A comparison between the values of the escape ratios from theoretical calculations and from the curve ($\eta = 0.0614/E - 0.00858 + 0.000347 \cdot E$) fitted to the experimental data. The error bars indicate one S.D..

Measurements of escape ratios

The detector used in this work was a 5 mm thick 80 mm² Kevex Si(Li)-detector with a FWHM of 158 eV at 5.9 keV. To avoid incomplete charge collection at the edge of the detector crystal, a Ta-collimator was placed in front of the detector thus reducing its effective sensitive area from 80 mm² to about 30 mm²¹¹. The geometry of the detector and the sample is shown in figure 1. Since the transmission through a 5 mm thick Si-crystal is less than 10^{-4} for X-rays with energies below 15 keV, escape from the rear of the crystal can be neglected. Compared to the mean free path of Si X-rays, the dimensions of the crystal can be considered as infinite.

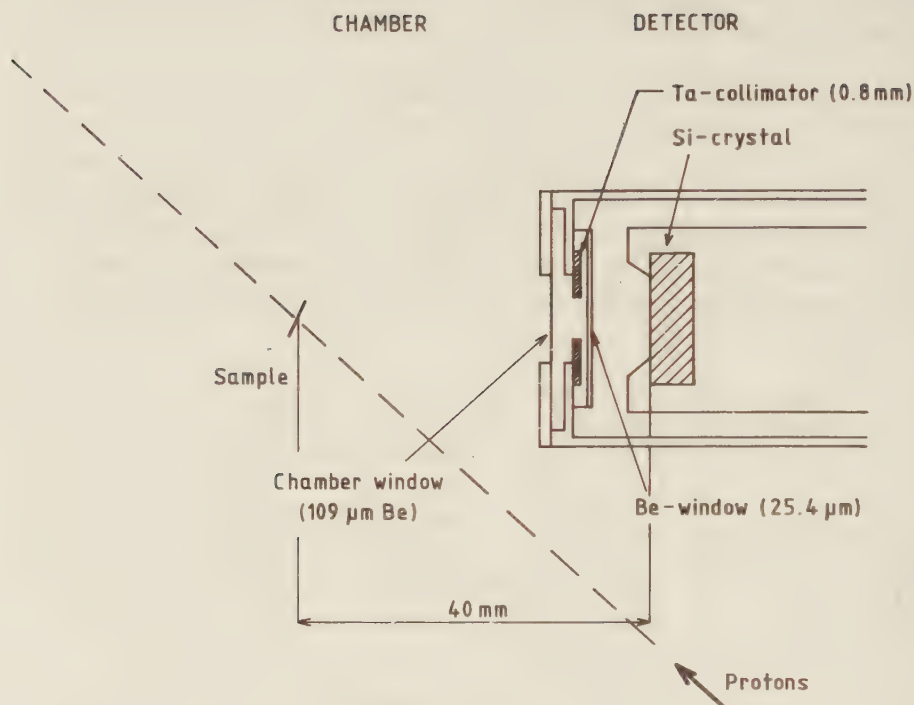


Fig 1. The geometry of the detector arrangement in the Lund PIXE set-up.

For the geometry shown in figure 1 and with an 8 mm proton beam collimator, the angles θ of all X-rays reaching the detector is less than 8° . Calculations of ϵ using formulae (1) and (2) respectively for this angle will give less than a 1% difference between the results. Hence, for the geometry in question, the dependence on angle θ can be neglected.

Thin homogeneous single element standard foils were irradiated to get good counting statistics in the escape peaks (normally > 5000 counts). The library of the HEX program was extended to include extra peaks for the escape peaks of interest. The escape peaks and the parent peaks were fitted independently using the HEX-program. In figure 2 the measured escape ratios η versus the X-ray energy of the full energy peaks are plotted. By using least squares fits, two

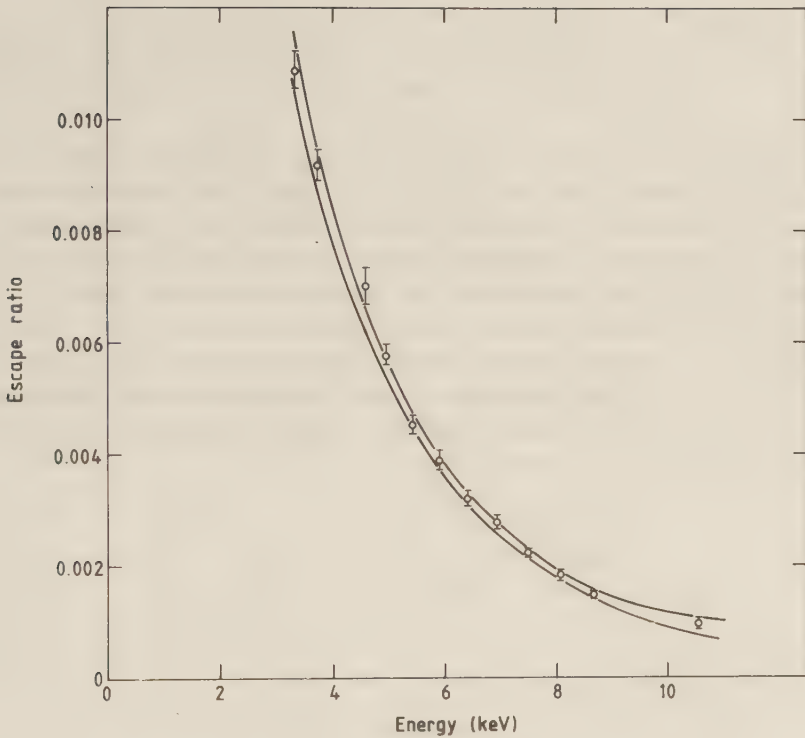


Fig 2. The measured escape ratios ($\pm$ one S.D.) as a function of the energy of the incident X-rays. In the diagram the 95% confidence interval around the fitted function $\eta = 0.0614/E - 0.00858 + 0.000347 \cdot E$ is also shown.

different curves have been fitted to the measured values. The first fit based on the physical model of the escape ratio is⁸

$$\eta = C_1(1 - C_2 E^{C_3} \ln(1 + 1/(C_2 E^{C_3}))) \quad E > 1.84 \text{ keV} \quad (3)$$

The values of C_1 , C_2 and C_3 found by the non-linear least squares fit were 0.0226, 0.0141 and 2.86. This value of C_1 (0.0226) should be compared to that used for the theoretical calculations ($C_1 = 1/2 \cdot \omega_k \cdot (r-1)/r = 0.0221$). The value of reduced χ^2 obtained from the fit was 0.695.

A simplified model

$$\eta = C_1/E + C_2 + C_3 \cdot E \quad 3.3 \text{ keV} < E < 10.6 \text{ keV} \quad (4)$$

was also fitted to our measured values (reduced $\chi^2 = 0.811$). This model can be compared to the model $\kappa = \eta / (1 - \eta) = C_1/E + C_2 + C_3 \cdot E + C_4 \cdot E^2$ suggested by Reed and Ware¹². The deviation of the results between the two fitted curves is shown in figure 3. Agreement in the energy interval of interest (3.3 - 10.6 keV) is very good with a maximum deviation of 2%. Since the statistical analysis is simplified and the deviation of the results in the two models so small, the fit of model (4) will be used in the following discussions. It is, however, impossible to use the simplified model outside this energy interval (see figure 3). The 95% confidence interval for the fitted values of the escape ratios η has been calculated and is also shown in figure 2.

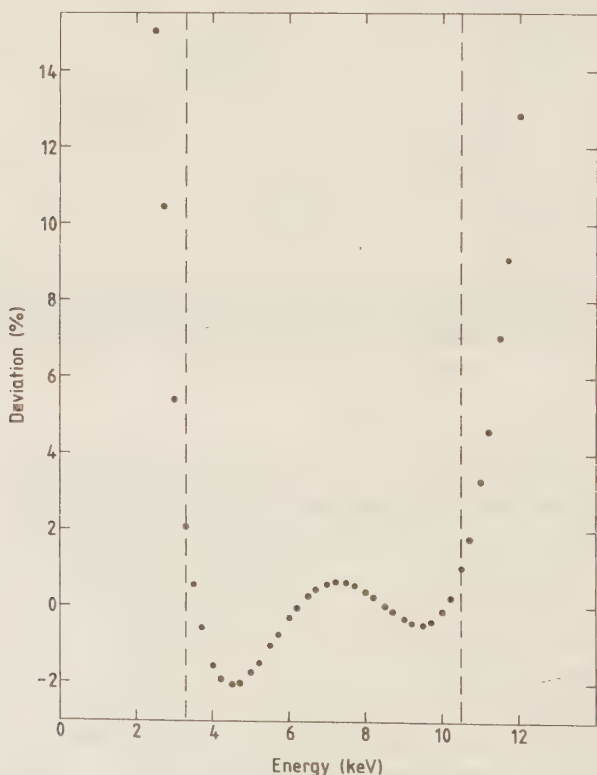


Fig 3. The relative difference between the escape ratios obtained from the two fitted curves $\eta = 0.0614/E - 0.00858 + 0.000347 \cdot E$ and $\eta = 0.0226(1 - 0.0141 \cdot E^{2.86} \cdot \ln(1 + 1/(0.0141 \cdot E^{2.86})))$ as a function of energy E .

In Table 2 the results from the fitted curve are compared to the theoretical values calculated.

The results of the determination of the relative intensities of the escape peaks to their parent peak (κ) are compared in Table 3 with results from refs. 7 and 13. Reed and Ware⁷ used a detector with an active area of 12.6 mm² and a depth of 3.64 mm and Sioshansi and Lodhi¹³ a 5 mm thick collimated 80 mm² detector (a set of two collimators 7 mm and 3 mm at a distance of 5.0 cm and 3.5 cm from the detector crystal was used). The agreement between the results of this work and those obtained by Sioshansi and Lodhi is excellent, except for potassium. For most elements the values from Reed and Ware are 10% or more lower. However, considering the uncertainties, the agreement is fairly good.

Detected K_{α} -line	The relative size of the escape peak		
	This work (fitted value)	Reed and Ware ⁷	Sioshansi and Lodhi ¹³
K	0.0111±0.00021		0.00985±0.00020 ($K_{\alpha}+K_{\beta}$)
Ca	0.00934±0.00016	0.0071±0.0003	0.00805±0.00040
Sc	0.00786±0.00012		0.00774±0.00008
Ti	0.00660±0.00009	0.0058±0.0002	0.00661±0.00020
V	0.00554±0.00007	0.0053±0.0002	0.00526±0.00010
Cr	0.00465±0.00006	0.0043±0.0003	0.00468±0.00007
Mn	0.00388±0.00005	0.0033±0.0005	0.00384±0.00008
Fe	0.00324±0.00005	0.0030±0.0001	0.00293±0.00006
Co	0.00269±0.00004	0.0021±0.0003	0.00273±0.00008
Ni	0.00223±0.00004	0.0017±0.0003	0.00229±0.00011
Cu	0.00185±0.00004		0.00175±0.00005
Zn	0.00153±0.00004	0.0013±0.0004	0.00158±0.00006
As	0.00091±0.00007		0.00108±0.00006

Table 3. The size of the escape peak area to the full energy peak area for different elements. For comparison, the results from refs. 7 and 13 are given.

Escape peaks in the computer program

If the escape peaks in an X-ray spectrum are not fitted, erroneous results will occur because of the interferences between escape peaks from major X-ray lines and full energy peaks from minor components. An example is the iron content in a welding fume sample which gives rise to an escape peak at 4.66 keV, thus interfering with Ti which is often found in rather low concentrations in welding fumes. Another example is the problem of getting reliable results for phosphorous in biological material because of interference with the escape peaks of Ca K_{α} and K K_{β} . Using values of the escape ratios found by fitting the parameters of the simple model (4) described above, the size of the escape peaks relative to the parent peaks (κ) have been calculated for all X-ray peaks in the energy interval 3.3 - 10.6 keV. The ratios of the escape peaks at lower energies are of less interest since X-ray peaks are not detected in that energy region. The size of the escape peaks from X-ray lines above 10.6 keV is usually small due to decreasing cross sections for the production of X-rays in the sample and decreasing escape ratios with increasing X-ray energy.

The relative intensities of the escape peaks to their parent peak (κ) are added to the information on the peaks in the HEX library. Since the computer program works from higher to lower X-ray energies in constructing the physical model, the following technique suggested by Reed and Ware^{1,2} is used: An image of the X-ray peak modelled multiplied by the relative size of the escape peak is added to the model at an energy 1.74 keV below the parent X-ray peak. This is a very fast and convenient way of including the escape peaks in the computer fit. It gives peaks with correct transmission and area but of a somewhat erroneous width. The difference in FWHM is, however, so small (e.g., for Fe K_{α} the difference is about 20 eV) that for practical analytical work it can be neglected.

PILE-UP PEAKS

When two photons reach the X-ray detector within a certain time interval, the corresponding pulses will be fully or partially added in the amplifier. In the case of complete addition, pile-up peaks appear at an energy which is equal to the sum of the individual energies. The pile-up effect can be reduced by using an electronic pile-up rejector system, a beam deflection system or a combination of both systems. The system used in the Lund PIXE-facility for obtaining a

pile-up interval of about 250 ns is described by Malmqvist et al.¹⁴.

The count rate N of the pile-up peak emanating from adding pulses corresponding to X-rays of energy A and B is

$$N = 2\tau N_A N_B$$

The count rate of the pile-up peak when A is equal to B is

$$N = \tau N_A^2$$

where τ is the pile-up interval and N_A , N_B the numbers of pulses corresponding to X-rays of energy A and B per unit live time respectively.

To be able to calculate the size of a pile-up peak by using the formulae above or a more general formula suggested by Steinbauer¹⁵, the current has to be constant during the irradiation. The formulae also require a known pile-up interval τ .

To incorporate the pile-up peaks in the HEX fitting routine, another approach to the solving of the problem has been chosen which is not dependent on a constant count rate during the irradiation of the sample or a known value of τ . In figure 4 a flow chart of the technique used is shown. The first linear fit to the spectrum is performed without the pile-up peaks. The peaks are sorted and the i largest peaks selected for the continued calculations. The number i can be changed depending on the application. If the energies of two peaks differ less than 50 eV, they are considered as one peak. The relative intensities and energies are calculated for all the possible pile-up peaks (number of pile-up peaks = $1(i+1)/2$). The m largest pile-up peaks are then selected. The number m can also be varied. Knowing the relative intensities and energies of these m pile-up peaks, they can be added to the library of HEX as one special "pile-up element" including all the pile-up peaks chosen. By treating the pile-up peaks as a special element with fixed relative intensities between the peaks, the interferences with other X-ray peaks can be resolved. The relative intensity of each pile-up peak is adjusted by a factor to give correct results since in the fitting routine they will be regarded as normal X-ray peaks with transmissions

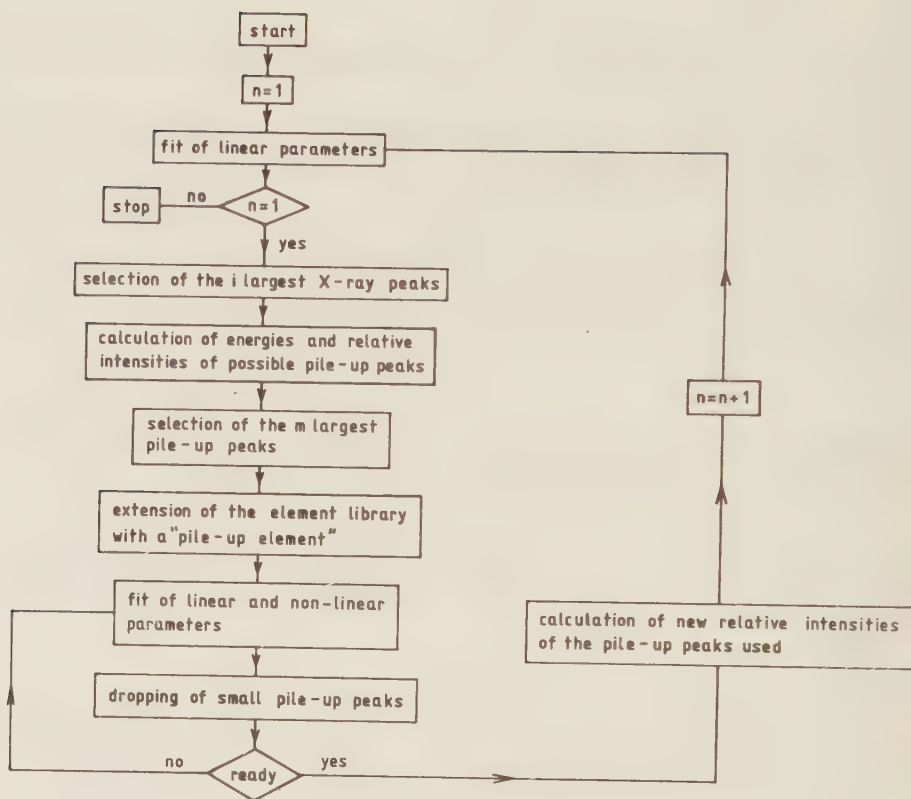
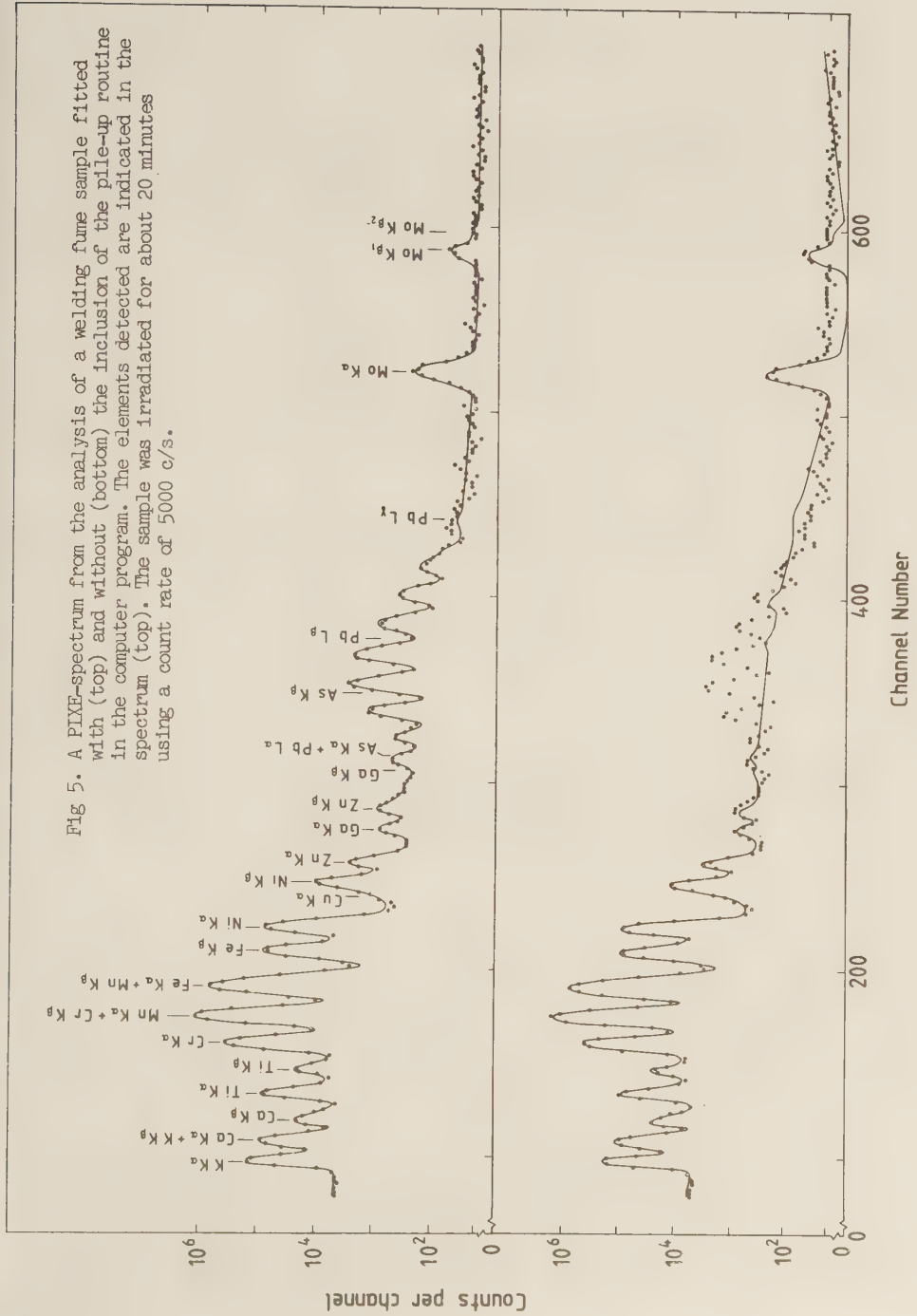


Fig 4. A flow chart of the routine used for fitting pile-up peaks.

different from those which the pile-up peaks have. In the following iterations, the "pile-up element" is treated exactly in the same way as other elements which have been requested, e.g., too small pile-up peaks are dropped. When one of the various conditions for finishing the fitting procedure is fulfilled (see above) and prior to performing the last linear fit, the relative intensities of the escape peaks are recalculated from the actual areas of the X-ray peaks and these updated values are used in the last linear fit.

Fig 5. A PIXE-spectrum from the analysis of a welding fume sample fitted with (top) and without (bottom) the inclusion of the pile-up routine in the computer program. The elements detected are indicated in the spectrum (top). The sample was irradiated for about 20 minutes using a count rate of 5000 c/s.



ELEMENT	AMOUNT($\mu\text{g}/\text{cm}^2$) (pile-up routine not included)	AMOUNT($\mu\text{g}/\text{cm}^2$) (pile-up routine included)
K	55.9	56.0
Ca	15.7	15.4
Ti	7.24	7.26
Cr	24.9	25.0
Mn	82.3	82.4
Fe	37.8	37.7
Ni	7.40	7.37
Cu	0.0738	0.0649
Zn	0.422	0.416
Ga	0.0897	0.0387
As	<0.021	0.0397
Rb	0.0904	<0.048
Mo	0.997	0.893
Pb	0.129	0.122

Table 4. The results of elemental mass calculations from the computer analysis of a welding fume sample (see figure 5) when the spectrum is fitted with and without the pile-up routine.

Experience of the fitting of pile-up peaks

The technique developed works very satisfactorily and has significantly improved the HEX-analysis. An example of a spectrum fitted with and without the pile-up peak routine is shown in figure 5. The sample (welding fumes from stainless steel welding collected on a Millipore filter) was irradiated for about 20 minutes. The count rate was about 5000 c/s and a beam deflection system having a 400 ns pile-up interval was used. The spectrum can be considered as being extremely complicated in having many almost equally large X-ray peaks. For the fit, the 40 largest pile-up peaks originating from the 12 largest X-ray peaks of the spectrum were used. The fitting of the spectrum can, in this particular

case, be improved further by including even more pile-up peaks. The difference between data and fitted values around channel 440 is an example of missing pile-up peaks ($\text{Fe}_\alpha + \text{Ni}_\beta$ and $\text{Fe}_\beta + \text{Ni}_\alpha$). In Table 4 are presented results from the two computer analyses. It should be observed that only elements frequently appearing in welding fume samples were asked for in the request list. Analysing a completely unknown sample, even more false elements would have been fitted if the pile-up peaks had not been included in the computer code. In many applications a lower number of pile-up peaks is sufficient to obtain a good fit.

The expected value of the energy of a pile-up peak is the sum of the energies of its two parent peaks. The pile-up peaks in figure 5 are, however, observed at somewhat higher energy (+30 eV). The apparent increase in energy for pile-up peaks in our set-up may be explained by a negative pedestal observed on the pulses at the output of the main amplifier.

The combination of good electronics to suppress pile-up peaks and an effective computer program to handle the remaining peaks facilitates the use of an increased count rate.

PEAK DROPPING

To obtain a good fit of an X-ray spectrum, all possible elements for the kind of sample analysed have to be included in the request list of the computer program. This will, however, normally cause the program to fit a lot of extremely small peaks which is very time consuming. A routine for dropping small peaks is therefore included in the computer code. In earlier versions of HEX, all peaks containing less than four counts were deleted from the list of the energies of the peaks. The peaks dropped are not fitted in the next iteration and computer time significantly reduced. This way of dropping peaks can, however give rise to erroneous results, e.g., if all but one peak of an element has been dropped and this remaining peak interferes with another element. Such problems have been observed for Mo and S, when all Mo peaks except one L-peak are dropped. The Mo peak may then get too large value at the expense of the S peak.

To avoid this kind of problem, the dropping subroutine has been improved. Two suitable peaks (e.g. K_α and K_β) from each element are marked not to be dropped unless the entire element is dropped. This way of dropping peaks works satisfactorily in reducing the number of peaks and still largely avoids the problems described above.

PLANNED IMPROVEMENTS

The HEX program was originally developed for thin target analysis, but it is now also used routinely for determining the peak areas of different elements in thick samples. For all matrices of interest, special libraries with adjusted relative intensities of the peaks are calculated. A special computer program TJOCKT¹⁶ is then used for evaluating the elemental composition of the sample. To make routines to handle thick samples easier and faster, the inclusion of this thick target procedure in the HEX program is planned.

A problem still not completely solved in the HEX program is that of the low energy tails on the X-ray peaks. As discussed above, the detector crystal is collimated to a sensitive area of about 30 mm^2 . This collimation reduces the tails significantly¹¹ but small non existent peaks may still be fitted close to a large X-ray peak to compensate for the remaining tail. We plan to make changes in the program so as to include the tails in the physical model. Different ways of handling the tails have been suggested in the literature^{17,18,19,20}.

SUMMARY

The HEX program has been improved by including escape peaks and pile-up peaks in the computer code and developing an effective routine for dropping very small X-ray peaks.

The measured escape ratios are in good agreement with theoretical calculations and the findings of other experimental groups. The computer code works by subtracting the escape peak from the X-ray spectrum as an image of the parent peak, giving very accurate analytical results.

The relative intensities and energies of the largest pile-up peaks are calculated and fitted to the spectrum as a special "pile-up element". This approach works independently of count rate and the setting of the electronics for pile-up suppression. Since the relative intensities of the pile-up peaks are fixed, interferences with other peaks can be resolved. The inclusion of pile-up peaks in the computer code facilitates the use of an enhanced count rate and thus a higher analysis speed.

ACKNOWLEDGEMENT

I am indebted to Mr H.C. Kaufmann, Tallahassee USA, for his many creative ideas and his active participation in the initial phase of this project. Dr K.R. Akselsson has been a never-ceasing source of ideas and stimulation throughout the whole work, for which I am indeed grateful. I am also very grateful to Mr K. Malmqvist for many helpful discussions about this work.

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CHARACTERISTICS OF WELDING FUMES

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ABSTRACT

The aerosols from 13 common electric arc welding processes have been characterized regarding total mass emission, particle size distribution, elemental composition and, when applicable, the oxidation state of chromium. The characterizations have been performed systematically for different combinations of welding current and welding voltage.

INTRODUCTION

In the work environment electric arc welding is a common process producing complex and abundant fumes. Since the distribution in size and elemental composition of the produced particles also vary within wide limits for different modes of operation, the finding of dose-response relations, the design of effective monitoring programmes and the choice of strategies for elimination techniques constitute a challenging task for industrial hygienists, epidemiologists, toxicologists, etc.. A fundamental prerequisite for the successful tackling of these central tasks is a thorough knowledge of the size distribution and composition of the welding aerosol particles. Although not dealt with explicitly in this work, in this connection other environmental factors, e.g. gaseous emissions, electromagnetic radiations and ergonomic aspects are of the outmost concern.

In a recent book, Moreton and Falla¹ have summarized existing information in the field of analysis and sampling of welding fumes while in a volume from the American Welding Society² the results of a major study of fumes and gases in the

the welding environment are reported. It is well known from other studies of welding aerosols that variations in current and voltage can influence the characteristics of the welding fumes produced^{3,4,5}.

To verify and extend existing information on welding aerosols, a comprehensive investigation of the total mass emission, particle size distribution, elemental composition and, when applicable, the oxidation state of chromium has been performed for 13 different welding methods (Table 1). The methods were chosen in cooperation with representatives of manufacturers and other experts on welding techniques and cover the three main types of welding: Shielded Metal Arc Welding (SMAW), Gas Metal Arc Welding (GMAW) and Gas Tungsten Arc Welding (GTAW). Most methods have been chosen from a Swedish firm manufacturing welding material, ESAB, which has an extensive export to the world market. In Table 1 the corresponding AWS classifications are, when possible, given.

Electrode	Type	Coating	AWS ^{a)} -class.	Diam.(mm)	Gas
1 OK 38.65	SMAW	iron powder, low hydr. zirconium added	E 7028	3.25	+
2 OK 38.85	SMAW	iron powder, low hydr.- rutile	E 7028	5	+
3 OK 38.95	SMAW	iron powder, low hydr. zirconium added	E 7028	4	-
4 OK 48.00	SMAW	iron powder, low hydr.	E 7018	2,3.25,4	-
5 OK 61.41	SMAW ^{b)}	rutile	E 308 L-15	3.25	-
6 OK 63.35	SMAW ^{b)}	low hydrogen	E 316-15	2.5,3.25,4,5	-
7 OK 69.21	SMAW ^{b)}	low hydrogen-rutile	-	3.25,4,5	-
8 OK 12.51	GMAW	-	E 70 S-6	1.2	CO ₂
9 OK 16.32	GMAW ^{b)}	-	ER 316 I S1	1.2	Ar
10 OK 16.32	GMAW ^{b)}	-	ER 316 I S1	1.2	Ar/CO ₂
11 OK 18.01	GMAW ^{c)}	-	ER 1260	1.2	Ar
12 OK 18.13	GMAW ^{c)}	-	ER 5154	1.2	Ar
13 Tungsten Th added	GTAW ^{b)}	-	-	-	Ar

a) AWS-class. = American Welding Society classification.

b) welding on stainless steel; c) welding on aluminium.

Table 1. A list of the welding methods included in this study. The numbers are used for identification in the various figures.

Since size distributions and elemental compositions have been investigated for several sets of current and voltage for each of the 13 methods of welding studied, an extensive database has been created. In this paper the results are summarized. A complete listing of the results can be obtained from the authors⁶.

MATERIAL AND METHODS

SAMPLING EQUIPMENT

Figure 1 shows the design of the sampling arrangement. The welding takes place beneath an aluminium hood. Two fans (ESAB, OFA, 13 kPa at 60 m³/h) connected in series pull air through a glass fibre filter (Millipore AP, 2529325, diam: 293 mm) on top of a pipe connected to the hood, in which the welding fume is collected. This equipment allows reproducible and representative sampling of fume from manual and automatic welding processes. The low velocity of the air around the welding point (<0.15 m/s) assures that the sampling procedure has no significant impact on the welding process and aerosol formation.

The total mass of welding aerosol is determined by gravimetric analysis of the glass fibre filters. These are insensitive to relative humidity and static electricity and hence repeated weighing over periods of several weeks give variations well below 0.1 % of the filter weight. For the collections in this study, the uncertainty in the total mass determinations is, in all cases, below 5%.

During the welding of a rod the filter will gradually clog and the pressure drop over the filter increase. The air flow then decreases and limits the amount of fume which can be collected on one filter. Tests have demonstrated the sampling efficiency to be above 95% for the collection of 1000 mg of welding fumes (fig. 2), which is quite sufficient for the sampling situations in the present study.

Due to diffusion, minor losses of small particles to the walls of the sampling equipment occurred. After a large number of collections (≈ 100) the pipe and hood were washed with distilled water and the water filtered. The filters and filtrates were analysed for iron (PIXE analysis). A comparison between the mass of airborne iron produced and the mass deposited on the walls indicates that losses from the wall are less than one per cent of the total mass of fume produced. In this determination, large globular metal spatter has not been considered.

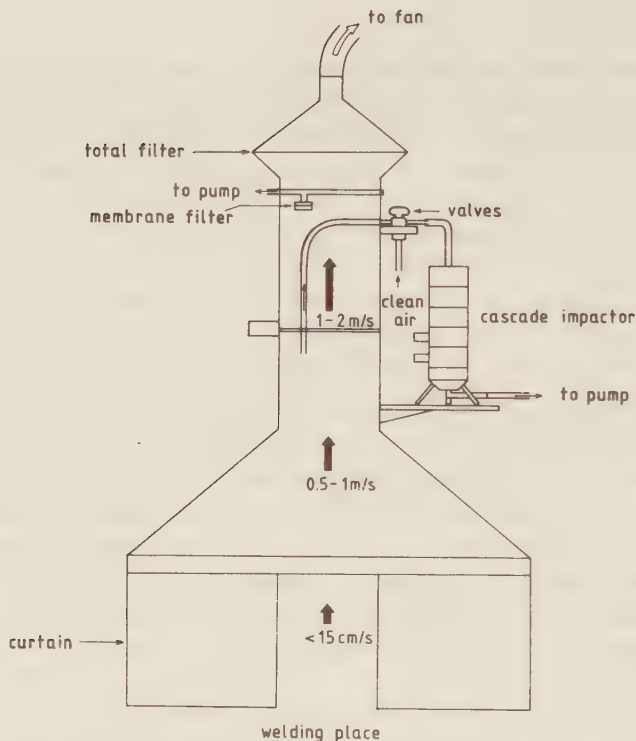


Figure 1. Sampling equipments for the characterization of welding aerosols. The arrows indicate the air velocity in different parts of the system.

The glass fibre filters are not well suited for chemical analysis since they contain high concentrations of impurities. Hence membrane filters made of mixed esters of cellulose (Millipore HAWP, diam.: 37 mm, pore diam.: $0.45\ \mu\text{m}$) have been used for determining the elemental composition of the aerosol. These filters contain insignificant concentrations of the elements of interest. A small portion of the total aerosol ($<0.5\%$) is collected on the membrane filter for subsequent elemental analysis. To check for possible variations due to the filter orientation, three filters were placed in different positions inside the pipe facing the air stream. While welding, sampling was performed simultaneously with all three filters and the relative elemental composition was determined for each of them. The compositions of the three samples agreed well within 5%. Since the filter efficiency is approximately 100% for all particle sizes⁷, the samples collected should be representative of the welding aerosol. However, due to the difference between the face velocity through the filter and the velocity in the tube, too many large particles will be collected from the aerosol. According to formulae given by Davies⁸, the oversampling of particles with an aerodynamic

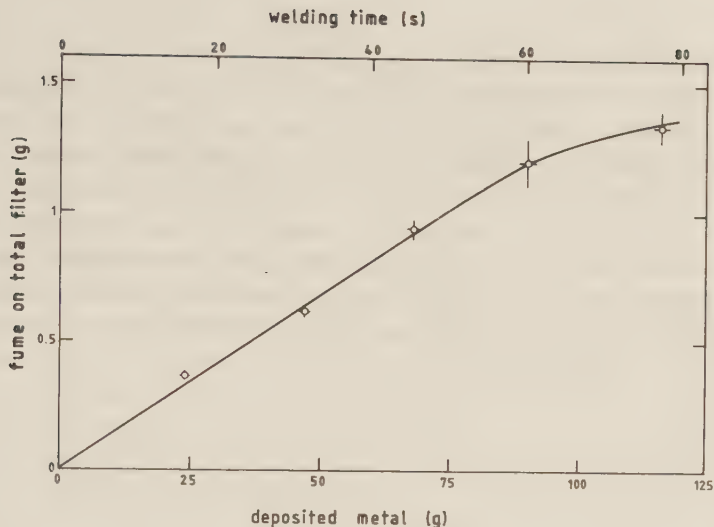


Figure 2. Performance of total fume sampling. Welding was performed with coated electrodes (OK 48.00) with a core diameter of 6 mm and a welding current of 300 A DC, reversed polarity. The error bars show one standard error of the mean.

diameter of less than 5 μm will be less than 10% and in previous studies^{3,9} it has been shown that welding aerosols contain very few large particles (more than 95% of the mass represents particles with aerodynamic diameters less than 1 μm).

Since the membrane filter is used only for determining chemical composition, oversampling of certain fractions of particle sizes will only be important if different particle sizes have different compositions.

To determine the particle size distribution, a probe was inserted into the pipe facing the air stream to collect a small sample of the welding aerosol into a Battelle-type cascade impactor¹⁰ placed outside the pipe wall. The nominal air-flow of this single orifice impactor was 1 litre/minute. The diameter of the probe was only 4 mm and to secure representative sampling, the sampling probe was allowed to move in a spiral back and forth over the entire cross section of the pipe. Several spirals were completed within a sampling period (30-60 seconds).

Since very dense aerosols are produced during welding and since the particle sizes which deposit on the two last stages in the impactor are predominant, the welding aerosol was diluted (1:10) by clean air (air drawn from outside the

building) before entering the impactor. Consequently the air velocity in the sampling tube from the probe will be low and diffusion losses of small particles will occur as will, sedimentation losses of large particles in the horizontal part of the tubing. These losses have been calculated¹¹ and are shown in fig.3. Since Reynolds number (Re) was about 50, i.e. well below the limit for turbulent flow ($Re \approx 2300$), the losses have been calculated assuming laminar flow with no turbulent mixing. Although by restricting sampling to an interval of from about 0.01 to 3 μm these losses represent limiting factors, as was mentioned above, these particle sizes constitute more than 95% of the mass of the welding aerosols.

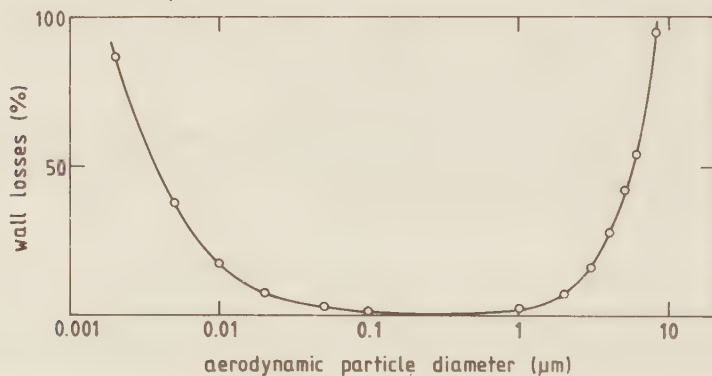


Figure 3. Calculated wall losses in the impactor tubing plotted versus particle diameter¹¹.

Similarly to the membrane filter the impactor probe samples subisokinetically. However, the oversampling (which occurs for particles with aerodynamic diameters larger than 5 μm), is insignificant since because of sedimentation any such particle, will not be able to penetrate the impactor tubing (see fig 3). Although the aerosol was diluted, for reasonable sampling times, some risks of overloading will still remain. Since even a slight overloading of the collection plates can severely alter the collection characteristics of a stage, further improvements have been carried out. By rotating the impaction plates off-axis during sampling, the particles are made to deposit over a larger area (30-60 times larger). This results in a significant improvement in collection performance and also facilitates accurate PIXE-analysis. Further details of this impactor modification are given in ref. 12.

ANALYTICAL METHODS

A brief description of the analytical procedures will be given here, but for a more detailed discussion see refs.^{12,13,14,15}.

The elemental composition of the welding aerosol samples collected has been determined mainly with the multielemental analytical method Particle Induced X-Ray Emission analysis, PIXE¹². We have used protons (with an energy of 2.55 MeV) from an electrostatic accelerator to irradiate a sample (normal irradiation time 1-5 min). Vacancies are created in the inner shells of the atoms in the sample. When these vacancies are refilled, X-rays with energies characteristic of the atom from which they originate are emitted. Measuring these X-rays with a semiconductor detector (Si(Li), sensitive area = 10 mm², FWHM = 160 eV at 5.9 keV) in combination with suitable electronics will yield simultaneous quantitative results for all elements heavier than about phosphorous, with detection limits of the order of nanograms (1 ng = 10⁻⁹ g). In fig.4 is shown an example of a typical X-ray spectrum from the irradiation of a sample of welding fumes.

For the analysis of one important light element, fluorine, we detect simultaneously the gamma rays produced in the nuclear reaction ¹⁹F(p,αγ)¹⁶O using a large volume sodium iodide crystal (detection limit 100 ng)¹⁶. Thin fluoride targets of known thicknesses are used as standards for quantitative analysis.

Since in this investigation, more than 3000 multielemental analyses had to be performed, access to the PIXE method with nuclear complementary techniques was a necessary condition for its realization. However, only the elemental composition is determined by the PIXE-method. Since in the case of chromium the oxidation state and probably also the solubility¹⁷ are of major importance in evaluating health hazards, a special analytical procedure¹⁵ was developed to quantify the masses of soluble and less soluble Cr(III) and Cr(VI). This procedure includes PIXE-analysis and complementary techniques such as Electron Spectroscopy for Chemical Analysis, ESCA¹⁸, a spectrophotometric method, DPC¹⁹ and transmission electron microscopy (TEM).

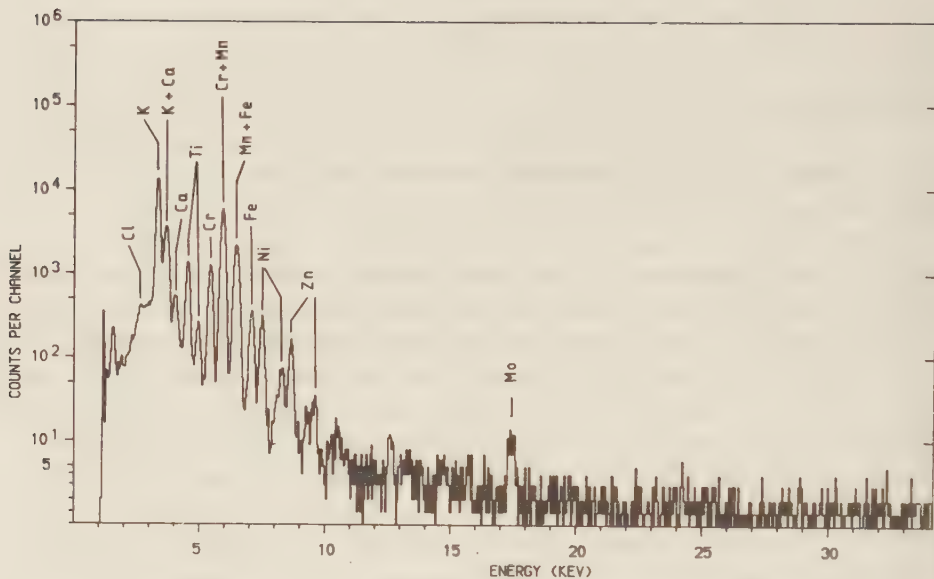


Figure 4. X-ray spectrum from the PIXE analysis of a welding fume sample (OK 69.21, I=140 A, U= 22 V) collected during stainless steel welding.

EXPERIMENTAL PROCEDURE

ANALYTICAL PROCEDURES

To determine the total masses of aerosols the pre-weighed glass fibre filters were re-weighed as soon as possible after collection. They were compared with pre-weighed blank filters to correct for possible systematic changes in filter weight. After weighing, a piece (3x3 cm²) was punched from the filter and then transferred to a sample holder (a 5x5 cm² slide frame). The samples were analysed by PIXE for about 60 seconds to determine the iron content per unit area of the filter. From this the total mass of iron on the filter can be determined and by comparison with the total mass of aerosol, as determined by weighing, the relative iron content can be calculated. Except in the case aluminium welds, the iron concentration was then used as a reference for determining the elemental composition on the membrane filters.

By scanning the filter area with a proton beam, the homogeneity of the aerosol deposit on the filter surface has been determined to be better than 3%. Since sample thicknesses may sometimes exceed 1 mg/cm², corrections for proton slowing-down and X-ray attenuation in the sample have been made. Taking this into account, the accuracy of the iron determination is typically 5%.

The membrane filters were weighed before and after sampling (using a Sartorius microbalance with a stated standard deviation of 1 μg). These filters were very sensitive to changes in relative humidity and to electrostatic build-up, although blank reference filters were used to correct for systematic weight changes due to the absorption of water and an α -emitting radioactive source and a piezo-electric decharger to reduce the effects of static electricity. Consequently, the gravimetric analyses were not sufficiently reliable for total aerosol mass determinations (the accuracy was in the interval from 10 to 30 %). The results were, however, used to double check the glass fibre filter determinations. After weighing, the filter was cut into two pieces one of which is glued to an aluminium frame which was mounted in a standard slide mount for PIXE analysis. The other half of the filter was stored in a Petri tray as a reserve sample. The sample was irradiated for 100 to 300 seconds with a proton current in the range from 5 to 50 nA using a proton beam area of 0.5 cm^2 . The masses of all elements heavier than sulphur were determined and during the proton irradiation the 6 to 7 MeV gamma-rays from the $^{19}\text{F}(\text{p},\gamma)^{16}\text{O}$ reaction were detected with a 5x4" NaI-crystal and counted for determining the fluorine content. While only 0.5 cm^2 of the total filter area was analysed during PIXE analysis, according to PIXE-measurements the aerosol deposit on the membrane filter was homogeneous within 2%, and hence the results were representative for the entire sample.

For stainless steel welding aerosols the chromium oxidation state was determined separately. Two parallel membrane filters collect aerosol in the pipe of the welding aerosol sampling set-up, giving mass differences between the two samples of less than 5%. A sample thickness from 0.05 to 0.1 mg/cm^2 is optimal for the analytical methods applied. One of the filters was washed with de-ionized water buffered with a solution of $\text{NH}_4\text{NO}_3/\text{NH}_4\text{OH}$ to pH 7.4. One half of each filter, unwashed and washed respectively, was analysed with PIXE to determine the total and the less soluble chromium. The other halves of the filters were analysed with ESCA¹⁸ which determines the oxidation state of the chromium in a 2 nm thick surface layer of the particles. To evaluate if the ESCA results were representative, another pair of parallel samples was taken and the individual welding aerosol particles were studied by transmission electron microscopy. The buffer solution containing the chromium which has been leached out was analysed with spectrophotometry using the DPC-reagent (diphenylcarbazide)¹⁹.

In the cascade impactor for particle size determinations glass plates (Casella, diam: 25 mm) were used. Prior to use, these were cleaned and dipped into a

solution of polystyrene in toluene, which was then drained through a valve, slowly and at a constant speed. After drying a $30 \mu\text{g}/\text{cm}^2$ thick polystyrene layer covered the plates. The plates were then placed 3 cm above a bath of melted hot paraffin (180°C) and the paraffin vapour allowed to condense on the plates for 15 min, forming a "sticky" layer to reduce "bounce-off" of particles²⁰. The glass plates were placed in the cascade impactor with the last four stages having 50 % cut-off diameters of 2, 1, 0.5 and $0.25 \mu\text{m}$, respectively, followed by an after-filter (Nuclepore, diam.: 25 mm, pore diam.: $0.4 \mu\text{m}$) to collect the smallest particles. After sampling, the plates were slowly put into de-ionized water and the polystyrene coatings with the aerosol samples floated off on to the surface of the water whence they were transferred to our standard aluminium frames. The latter were then mounted in the slide frames for subsequent proton irradiation for about 100–200 seconds, using a beam current of 50 to 150 nA and a 0.5 cm^2 beam area, sufficient to cover the samples completely. For the after-filter, the beam area was 0.13 cm^2 with a proton current of 30 to 50 nA and the analysis times from 200 to 300 seconds. Fluorine in the impactor samples was determined using the $^{19}\text{F}(p,\alpha\gamma)^{16}\text{O}$ reaction.

SAMPLING PROCEDURES

In Table 1 the different welding situations studied are summarized. The welding current was varied within the intervals recommended for each method and dimension by the manufacturer. The welding voltage was varied significantly outside "proper" welding conditions in order to show any possible systematic dependence of fume production on welding voltage.

Three to five collections were made for each set of welding parameters. The results are given as averages of the numbers of measurements made and the error limits given are one standard error of the mean. For some methods, e.g. GMAW on aluminium, only very restricted parameter intervals can be used for welding. The alternating current mode is recommended only for a few SMAW-methods and hence the influence of current mode on the welding aerosols has been studied for these methods only.

For the direct current SMAW-methods, an ESAB 400 welding generator is used in accordance with the instructions by the welding electrode manufacturer, i.e. reversed polarity (electrode positive). The welding is performed manually by a skilled welder exerting himself to maintain constant welding conditions.

Normally, the fumes from only one electrode are collected on one glass fibre filter but, to reduce weighing errors, for a few methods with very low fume emission several electrodes were welded. Current and voltage were recorded on a two-channel chart recorder. Voltage was measured between the electrode and the work piece and the current by a precision resistor in series with the welding generator. When AC-welding is carried out, a high current transformer was used.

For the GMAW-methods, an ESAB LBA 550 welding generator was used with the welding gun mounted in a fixed position perpendicular to the workpiece. The latter was clamped to an aluminium wagon running on rails with a very constant but variable speed to simulate the normal movement during welding. This automatic welding arrangement is necessary for the semi-automatic methods studied, since it is difficult to maintain constant conditions manually. Current and voltage were recorded in the same way as for the SMAW-methods. The wire feeding speed in GMAW-welding is adjustable and the setting was noted for each welding situation. They were calibrated by feeding the wire without welding for a certain time and measuring the amount of wire fed. The protective gas flow was monitored by a rotameter.

For GTAW-welding, a Miller DC welding generator is used. Due to the low emission rates from GTAW-processes, very long welding and collection times (30-40 min) were used.

The fans which pull air through the sampling pipe and the pumps for the membrane filter and the cascade impactor were all started before welding starts. After about 10 seconds of welding, the valves in the connections for the impactor are switched from clean air to welding aerosol collection, which continues for 20-40 seconds. The valves are then switched back and all the aerosol still inside the cascade impactor is allowed to be collected at nominal flow rates before the pump is turned off. About 20 seconds after finishing the welding, the fan and pump were turned off and the filters and impactor plates exchanged in a laboratory completely sealed-off from the welding hall.

RESULTS AND DISCUSSION

TOTAL FUME EMISSION

To facilitate comparison of fume production from different welding techniques, it is convenient to define two entities, viz. the total fume emission rate, E, the total mass of emitted fume in g/min, and the relative fume formation index, R, the total mass of emitted fume normalized to the mass of deposited consumable (excluding slag) in mg fume per g deposited consumable. In Table 2, the total masses of aerosols produced in the different welding processes, expressed in terms of E and R, are summarized. The results selected are for "normal" values of welding parameters and dimensions.

Electrode	Diam.(mm)	I (A) ¹	U(V) ¹	E(g/min)	R(mg/g)
OK 38.65	3.25	160	35	0.58	16.7 ³
OK 38.85	5	300	34	1.30	15.7
OK 38.95	4	210	32	0.93	21.7
OK 38.95 ²	4	205 ²	30 ²	0.75	19.2
OK 48.00	3.25	140	23	0.45	26.0
OK 61.41	3.25	115	33	0.38 ³	11.3 ³
OK 63.35	4	140	24	0.39	15.6 ³
OK 69.21	4	140	22	0.29	12.4
OK 12.51 CO ₂	1.2	180	30	0.23 ⁴	5.4 ⁴
OK 16.32 Ar	1.2	180	26	0.20	3.8
OK 16.32 Ar/CO ₂	1.2	180	26	0.29 ³	5.7
OK 18.01 Ar	1.2	180	22	0.49	20.5
OK 18.13 Ar	1.2	160	24	0.91	24.1
Tungsten, thoriated	-	112	12	0.002	-

1) Direct current; reversed polarity (electrode as anode).

2) Alternating current.

3) Standard error of the mean : 5-10%.

4) Standard error of the mean : 10-15%.

Table 2. The welding situations referred to in the text as "normal" welding, implying that the welding currents were chosen to be in the middle of the intervals recommended by the manufacturers and the welding voltage close to the values recommended. E and R denote respectively the fume emission rate and the relative fume formation index. The standard errors of the mean were less than 5% if not given.

The total fume emission rate is very dependent on electrode dimension and electric power and, due to variation in these parameters, E varies in the interval 0.2 to 2 g/min for the methods in the present study (except for GTAW). As can also be seen from Table 2, large variations in R are found between the different methods (3-35 mg/g). The choice of welding method will strongly influence the ratio between fume production and welding production. However, since this choice is guided also by technical demands and availability and since the comparison does not include the chemical composition of the welding aerosol, it is not always possible or even desirable to choose the method of lowest relative fume formation index. From Table 2 can be inferred that the SMAW methods generally give higher values of both E and R than the GMAW methods. One exception, however, is GMAW for aluminium welding with equally high or even higher values than SMAW.

The results in Table 2 can be compared with those of the systematic study in ref.². The methods in this study with a corresponding or very similar method as in ref.² are OK 48.00, OK 61.41, OK 63.35, OK 12.51, OK 16.32 and OK 18.13. Both E and R for these methods are in good agreement with the results in ref.², the differences being normally smaller than 10%. The discrepancies might be explained by somewhat different welding conditions and variations between different brands of welding consumables of the same classification.

SMAW

In Table 2 are given emission results for "standard" welding situations recommended by the the manufacturer. However, when the welding current is raised within the intervals recommended, there will be a significant increase of E reflecting the enhanced melting rate of the consumable. This current dependence seems similar for all SMAW-methods and in fig 5 the fume emission rate is plotted versus welding current (at normal welding voltage). All the methods, dimensions and currents studied are included and it seems that E might be expressed mathematically as $E = a \cdot I^b$. Regression analysis of this power curve gives $a = 2.1 \cdot 10^{-4}$ and $b = 1.54$ with $r^2 = 0.88$, indicating a strong dependence of E on current. Since all the data points in fig 5 lie close to the regression line, the seven SMAW-methods in this study, despite their different dimensions, coatings and core compositions, seem to follow approximately the same current dependence when they are used according to the manufacturer's recommendations. These results agree well with those of refs.² and 21.

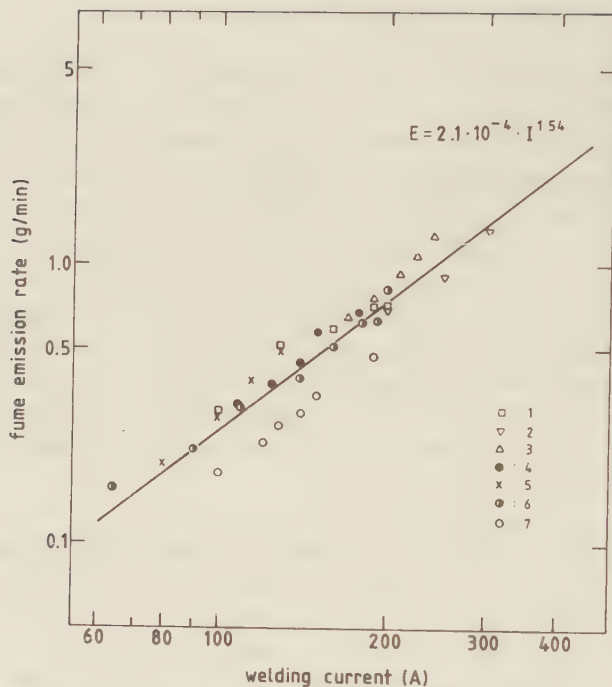


Figure 5. Fume emission rates for all the SMAW-methods in this study plotted versus welding current ($r^2=0.88$). The number at each symbol refers to the corresponding welding method in Table 1.

For the relative fume formation index R , the influence of welding current is, within the stated current interval, normally rather low, since the increased fume emission rate is mainly the result of an increased melting rate. For some methods, a slight increase in R with current is found, probably because of the increased temperature at the melting tip of the electrode.

In fig 6 and 7 the fume emission rate and the relative fume formation index of three different SMAW methods (for stainless steel) are plotted versus welding voltage. Increases in both E and R are observed with increasing voltage. At high voltage the long electric arc creates increased turbulence and hence facilitates penetration of oxygen through the protective atmosphere formed by the evaporating electrode coating. This oxygen can react with the melted and vapourized metals forming oxides which will promote fume emission since they often have higher vapour pressure than the pure metals. From fig 7, it is evident that the influence of welding voltage on R is dependent of the type of

coating on the electrode in question. Different relations between voltage and arc length are the probable explanation for this. The crater formed by the coating during steady state welding hides part of the electric arc and hence it is very difficult to measure the arc length for direct correlation with R. Since the use of a longer arc causes increased disturbance due to metal spatter and turbulence it also produces a deteriorated welding joint. Hence, keeping the arc length short and welding voltage low, e.g. by keeping the angle between the electrode and the work piece close to 90° ²¹, should be recommended.

The SMAW methods in this study have normally been welded with DC and reversed polarity. For one method, however, AC is also recommended and in Table 2 E and R are given for this method for both modes of current. The values of E and R are somewhat lower in the case of alternating current but the differences (<10%) are insignificant from the hygienic point of view.

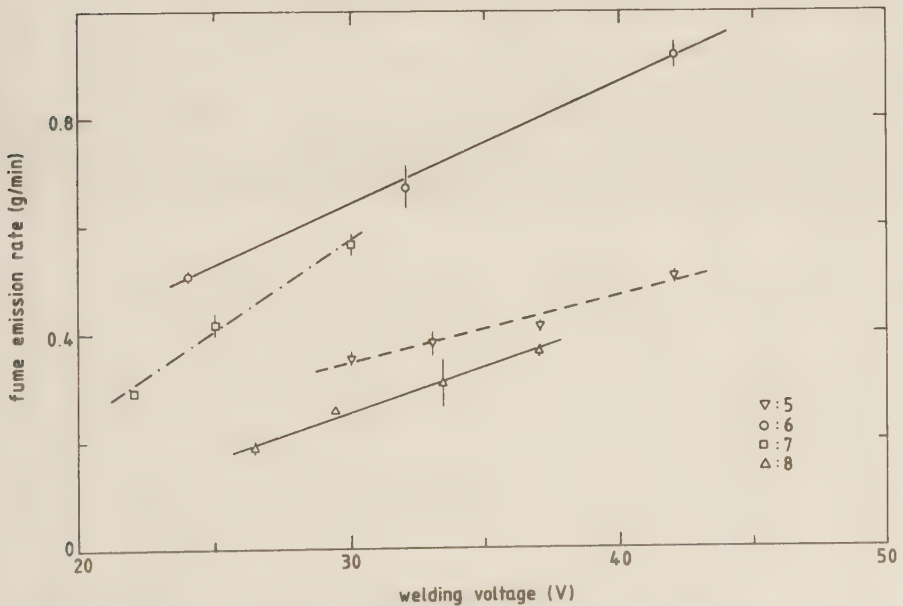


Figure 6. Fume emission rates for three SMAW-methods (stainless steel welding) and for the GMAW method with CO₂ as protective gas (mild steel welding) plotted versus welding voltage. The number at each symbol refers to the corresponding welding method in Table 1. The welding currents were 115, 160 and 140 A for methods 5, 6 and 7 respectively, and 200 A for method 8. The error bars show one standard error of the mean.

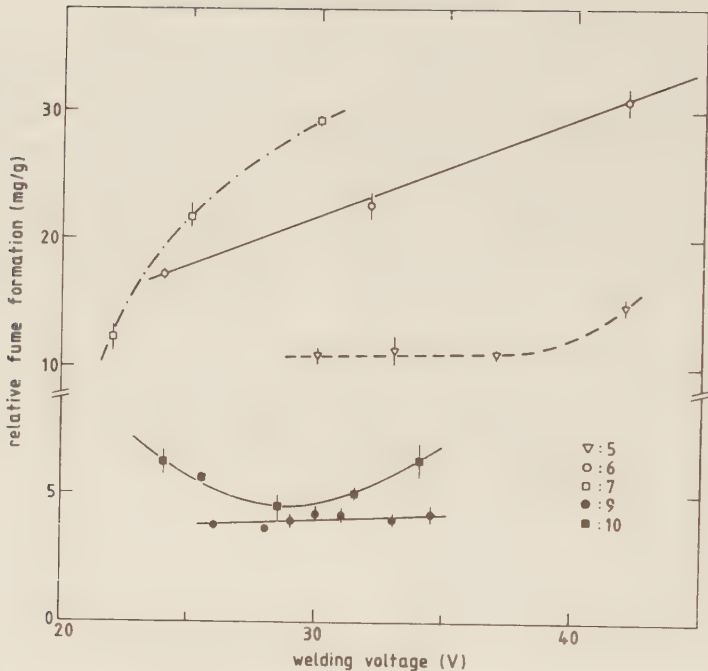


Figure 7. Relative fume formation index plotted versus welding voltage for the same SMAW methods as in fig. 6 and for the GMAW method with pure Ar (●) and Ar/CO₂ (■) as protective gases respectively. The number at each symbol refers to the corresponding method in Table 1. The welding current in method 10 was 180 A. The error bars show one standard error of the mean. Note the shift of scale on the ordinate axis.

GMAW

Semi-automatic methods for gas metal arc welding may appear to be well-controlled and simple physical systems composed of the melting metal wire and the surrounding protective gas. However, due to the influence of the protective gas on the electric arc and on the metal transport process, the fume emission will be a complex function of the welding parameters.

When pure CO₂ is used as a protective gas, the transfer of the melted metal from the electrode tip to the work piece can be characterized as large globules (diameter: 2 to 3 mm) transported by gravity and magnetic forces. The sizes of the globules are virtually unchanged when the welding parameters are altered. If, however, the protective gas is argon or mixtures of argon and CO₂, two different modes of transfer will be possible. With low voltage and low current the transfer will be globular with decreasing sizes and increasing numbers of

globules for increasing current. For high voltage, at a certain critical value of current, the transition current, a very abrupt change in the size and frequency of the globules takes place and metal transfer becomes a spray of very small droplets (diameter: 0.5-1 mm). The drop size remains rather constant when the current is increased and instead the number of droplets per unit time increases. The detachment of the small droplets from the electrode is due partly to the magnetic "pinch effect" and transport along the arc is due mainly to the plasma jet²². The value of current at which this transition occurs is proportional to the diameter of the electrode and dependent on the material and electrode extension²³.

When mixtures of argon are used, the gas with which it is mixed changes the properties of the protective atmosphere and hence the fume formation process will be altered. In fig 7 the relative fume formation index is plotted versus welding voltage with pure argon and with a mixture of 80% argon and 20% CO₂ as protective gases, respectively. While, for pure argon, R is rather independent of the welding voltage, there is a well-defined minimum at a specific voltage for the Ar/CO₂ case. The magnitude of R is also higher for all voltages when CO₂ is mixed into the gas and hence the oxidizing potential of the atmosphere surrounding the arc is increased. The oxides of several elements have higher vapour pressure than the pure elements, thus promoting fume formation in a oxidizing atmosphere. This effect has been shown in detail in refs.3 and 24.

The welding current for OK 16.32 in fig 7 ($I=180 \pm 5$ A) is above the transition level for this particular electrode with a diameter of 1.2 mm²⁵. To establish a stable spray arc, the voltage (arc length) has to exceed a certain value, which in the case of pure argon was about 30 V and for the Ar/CO₂ mixture 28 V. The minimum in R in fig 7 for the Ar/CO₂ mixture coincides with the lowest voltage at which a stable spray arc can exist. Once a stable spray arc is established, R will increase with voltage in case of Ar/CO₂ gas but remain constant for pure Ar. The increased voltage corresponds to a longer electric arc with a consequently longer residence time for the droplets in the oxidizing atmosphere while being transferred to the work piece, and hence, according to what is stated above, an increased probability for fume formation. The inert Ar-atmosphere which surrounds the arc protects the droplets from oxygen during transfer and essentially all fume will be produced, mainly due to vaporization, close to the melting tip where the temperature is very high.

In pure CO_2 -welding the fume emission rate increases strongly with voltage, as can be seen from fig 6. This dependence is in good agreement with the results of refs. 26 and 27, where the same or very similar welding parameters have been used. If, instead, the welding current is increased at constant voltage, the wire feeding speed increases with a decreasing length of the welding arc²⁶. In fig 8 the relative fume formation index versus current is plotted for constant voltage. Due to the decreasing transition time for the globules in the CO_2 -atmosphere, R decreases with increasing current (compare ref.3).

It is evident from the findings above that gas metal arc welding constitutes a complex field as far as the emission of welding fumes is concerned and that all welding parameters and conditions have to be stated precisely for adequate comparison of research results and finally that the choice of shielding gas has a significant influence on the fume emission characteristics.

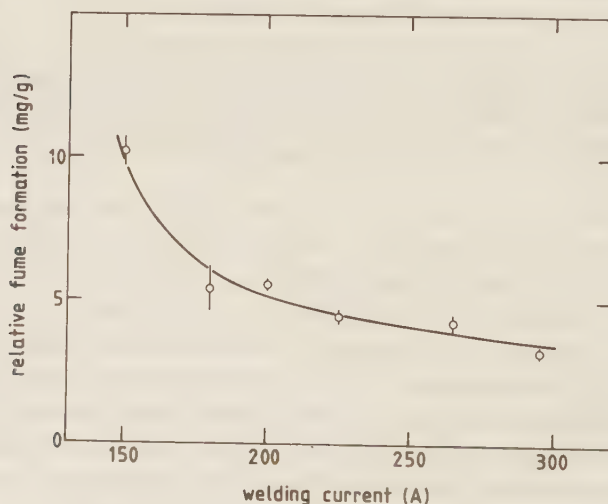


Figure 8. Relative fume formation index plotted versus welding current ($U=30$ V) for GMAW welding of mild steel with CO_2 as protective gas. The error bars show one standard error of the mean.

ELEMENTAL COMPOSITION

In Table 3, the elemental composition of welding aerosols from the different welding processes are given for the same parameter values as those in Table 2. The part of the aerosol which has not been analysed contains such elements as oxygen, nitrogen, sodium and silicon.

E l e m e n t s

	F	Cl	K	Ca	Ti	Cr	Mn	Fe	Ni	Cu	Zn	As	Rb	Zr	Mo	Pb
No. ¹																
1	7.1		8.8	2.6		.07	5.9	32		.08	.17 ³	.06 ³		.54		.10 ³
2	11	.26 ³	15	.62	.54		4.7	24			.29 ⁴					
3	11	.33 ³	15	2.0			3.4	23			.04 ³			.23 ³		.07 ³
3 ²	14	.54 ³	19	1.8			2.8	11			.04 ³			.36 ³		.07
4	16		16	9.5	.45	.04	3.7	19		.01	.13	.03 ³				
5	21		18	1.3	2.1	3.4	2.4	3.7	.22	.01	.25		.02			
6	24	.34	22	10	.62	3.1	2.7	3.3	.24		.11		.01		.03	.03
7	16	.20	22	3.5	2.3	3.0	14	3.4	.44 ³		.14				.09 ³	.04 ³
8						.07 ⁴	7.3	45		.26 ³	.04 ⁴					
9						10	5.3	28	4.5	.06	.17				.95	
10						12	4.8	31	4.8	.09	.18				.92	
11						.02 ⁴		.12 ⁴		.03						
12						.04	.14	.06			.02					

1) See Table 1; 2) Alternating current; 3) Standard error of the mean : 10-20%

4) Standard error of the mean : >20%

Table 3 . Relative elemental compositions (expressed as a per cent of the total mass of aerosol) of the welding fumes from the welding situations described in Table 2 as determined by PIXE analysis. The standard errors of the mean are less than 10% if not explicitly shown. Due to its low total emission GTAW is not included.

Basically, the elemental composition of a welding aerosol reflects the composition of the consumable electrode used insofar that the elements present in the welding consumable are also found in the aerosols but normally with their relative abundances altered. In the electric arc column the highest temperature is found at the axis near the melting tip of the electrode²⁸. Consequently, metal vapours will come mainly from the welding electrode and from the surface of the metal droplets being transferred in the arc. This statement is supported by the findings in ref.²⁹ in which a systematic study was carried out to

determine the site of aerosol production in SMAW-methods. Known concentrations of chromium, manganese and nickel were added to coating, core wire and workpiece respectively. By elemental analysis of the welding aerosol the contributions from the different sites were estimated, and the core wire was found to be the dominating source of these metals in the aerosol. One consequence of this finding is that the choice of work piece composition is not very critical in welding aerosol studies. It is, however, very important to check that no surface contaminations, such as metal primers, are present since they may be much more volatile and will contribute significantly although they emanate from the low temperature zone of the arc.

In Table 4 are given fractionation factors of the different metals in the welding aerosol relative to the welding consumable for four different welding methods. Noticeable are the high factors for manganese (2-7) while the factors of the other elements are well below unity. This is in good agreement with the results from the above study²⁹. Since manganese has a much higher vapour pressure than, e.g. chromium and nickel, it will also have a higher tendency to fume formation and occur in relatively higher concentrations in the welding fumes as compared to the work piece.

<u>Shielded metal arc welding</u>		<u>Gas metal arc welding</u>	
Low alloy electrodes <u>(n=4)</u>	Stainless steel electrodes <u>(n=3)</u>	CO ₂ - gas Low alloy steel (n=1)	Argon - gas Stainless steel <u>(n=2)</u>
Cr	0.17-0.21		0.68-0.70
Mn 2.2-6.1	2.3-3.8	6.9	4.2-5.2
Fe 0.22-0.33	0.055-0.066	0.49	0.47-0.50
Ni	0.025-0.040		0.36-0.41
Mo	0.027-0.052 (n=2)		0.24-0.32

Table 4. The elemental concentrations in the fumes divided by the elemental concentrations in the welding consumables. The intervals are defined by the minimal and maximal values. n = the number of methods included.

SMAW

The welding parameters, mainly the voltage, affect the elemental composition of the welding aerosol. In fig.9 are plotted the relative abundances of five different elements in the fume from a stainless SMAW-method versus welding voltage, showing increasing concentrations for the three core wire metals chromium, manganese and iron and decreasing concentrations of fluorine and potassium which originate from the electrode coating. For other electrodes, the voltage dependence is not exactly the same, but nevertheless the same groups of

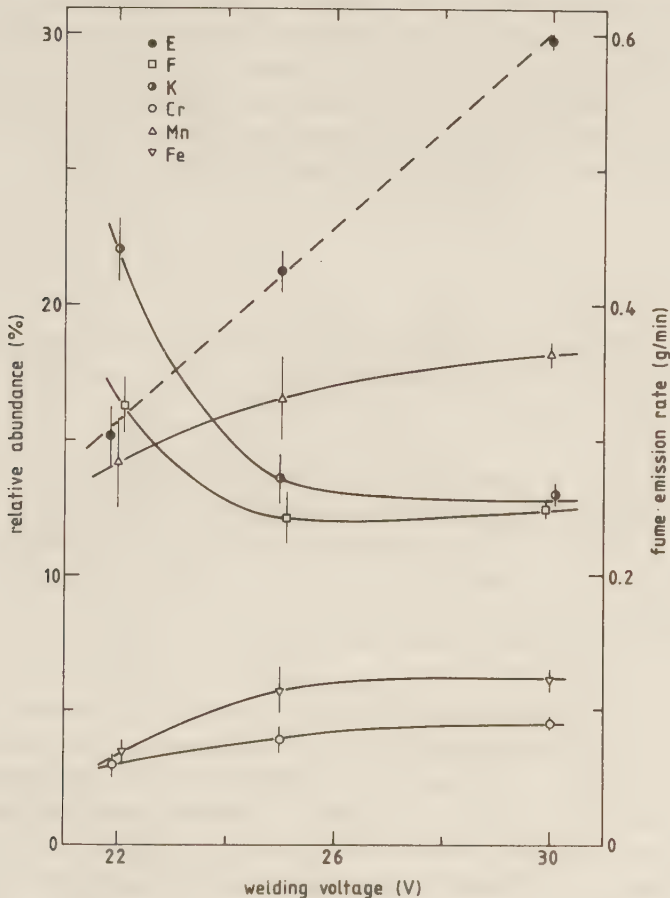


Figure 9. Relative elemental abundances (left-hand axis) in the fumes from welding stainless steel with a SMAW-method (OK 69.21, diam.:4 mm and I=140 A) plotted versus welding voltage. To facilitate estimating the absolute elemental emission, E is also plotted (right-hand axis). The error bars show one standard error of the mean.

elements develop, e.g. potassium and fluorine represent one category of elements following similar patterns of variation and chromium, manganese, iron and nickel normally another. The reasons for these variations may be the resemblance in chemical and physical properties and/or in the distribution of the elements in the electrode. The distinct voltage dependence of the elemental composition is probably explained by the variation in arc length. In fig.9 the dependence of the fume emission rate on voltage is also included in order to show how the absolute emissions of these elements vary with voltage.

Welding is normally performed in the DC mode and with reversed polarity but in some methods AC is also used. For one of the methods studied here, the change to AC causes a drastic change in the relative composition (compare Table 3). The temperature at the electrode tip depends on the polarity and consequently the use of an alternating current is expected to change the conditions for fume production and hence the chemical composition.

GMAW

In the semi-automatic GMAW-methods no protective electrode shielding is used and the composition of the welding fumes is determined by the composition of the metal wire and by the protective gas.

Gas metal arc welding of mild steel is normally performed in a 100% CO₂ atmosphere giving globular transfer as described above. When the welding parameters are varied, no significant variation in the elemental composition has been observed in the present study. This and the relative abundances of Mn and Fe observed are in good agreement with the results from other studies of the same process^{3,30}.

It was shown above that a protective atmosphere of argon affects the fume emission characteristics since metal transfer varies with welding parameters. In fig 10, it is shown that the same effect is found in the elemental composition. The relative abundances of two elements in the fume during the welding of stainless steel are plotted versus welding voltage (100% Ar - □, Ar/CO₂ = ◻). To allow estimates of the absolute mass emissions of the elements, the fume emission rate is also plotted. All metals except manganese have higher relative abundance with Ar/CO₂ than with pure Ar. For both protective gases, the general trend for both elements is to increase with voltage. However, in pure Ar gas, a

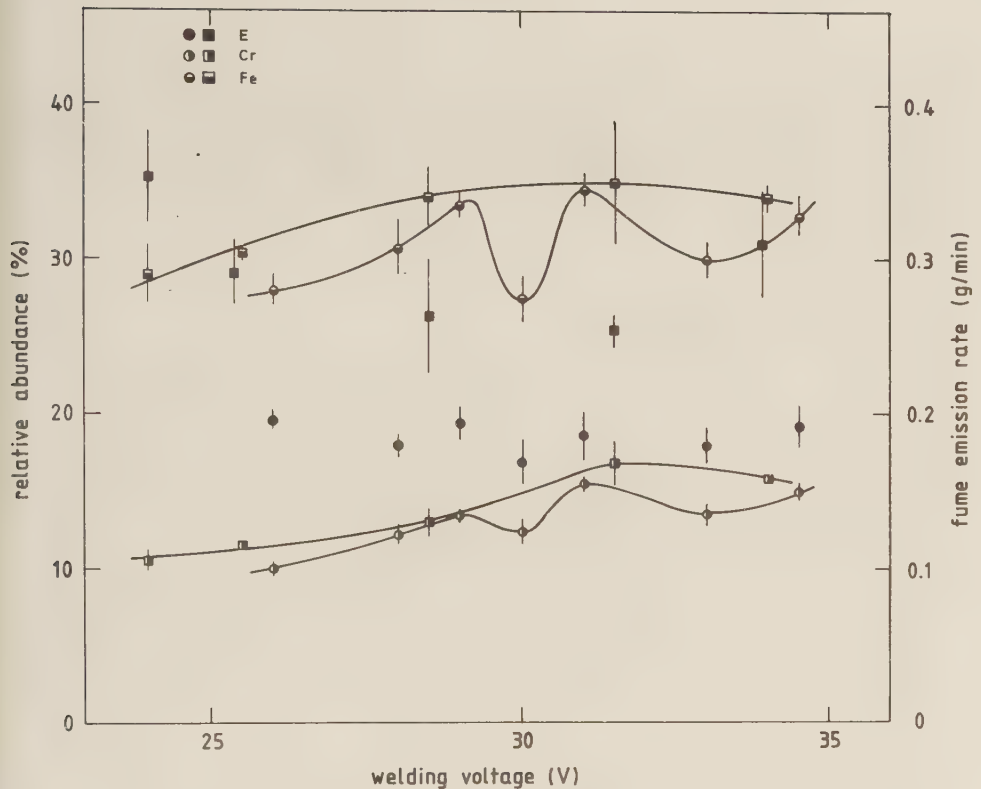


Figure 10. Relative elemental abundances (left-hand axis) in welding stainless steel with GMAW (OK 16.32, $I=180$ A) and 100% Ar (o) and Ar/CO₂ (□) as protective gases, respectively, plotted versus welding voltage. To facilitate estimating the absolute elemental emission, E is also plotted (right-hand axis). The error bars show one standard error of the mean.

fine structure with dips in the relative abundance at the lowest voltage (approx. 30 V) at which a stable spray transfer can exist is noticed. A similar dip is not observed at the corresponding voltage (approx. 28 V) in the case of Ar/CO₂. A tentative explanation for this fine structure and the difference between the gases is the establishment of a very stable arc essentially free from spatter and turbulence at a critical voltage, assuming the current is high enough, i.e. above the transition current. When pure Ar is used, the oxidizing agents come primarily from the surrounding air and their penetration is significantly reduced because of the very stable arc. With 20% CO₂ in the gas, the oxygen in CO₂ will be the dominant oxidizing agent and the influence of the surrounding air is less pronounced.

GTAW

Since the total fume emission is very low for GTAW and pure Ar as the protective gas, no results on the elemental composition of the aerosols formed are included in Table 3. However, apart from Fe, Mn, Cr, Ni, Cu and Zn, traces of W are also found.

OXIDATION STATE OF CHROMIUM

An analytical routine developed for determinations of chromium oxidation state¹⁵ was applied to stainless steel welding aerosols from three SMAW-methods and one GMAW-method. The results are shown in Table 5. For GTAW of stainless steel, the total fume emission was too low for this analytical procedure to be used. In aerosols from the three SMAW-methods for stainless steel welding, more than 50% of the chromium is soluble and hexavalent. Between 60 and 100 % of the chromium in the particle surface layers is hexavalent as determined by ESCA-analysis, but decreases after washing the aerosol with a buffer solution (pH 7.4). Apparently most of the hexavalent chromium on the particle surfaces leaches out during washing. The formation of hexavalent chromium is dependent on which elements have been added to the coating and it has been shown by Kimura et al.³¹ that it is possible to reduce the amounts of hexavalent chromium by changing the additives to the coatings and still perform technically adequate welding.

Method number ¹	Diam. (mm)	I(A)	U(V)	Cr-tot (%)	A	B	C
5	3.25	100	35	3.4	.50	.60	.27
6	3.25	100	22	4.4	.73	1.00	<.15
7	3.25	105	21	2.9	.52	1.00	<.15
9	1.2	180	26	12	.019	<.15	<.15

1)= see table 1

A = Cr(IV)-soluble/ Cr-total.

B = Cr(VI)/Cr-total on the particle surfaces.

C = Cr(VI)/Cr-total on the particle surfaces after washing.

Table 5. Results from determinations of oxidation state and solubility of chromium in welding aerosols from stainless steel welding.

Transmission electron microscopy (TEM) gives information on the structure of individual welding particles for interpreting the ESCA-results. The aerosol particles from the SMAW methods appear as chains or agglomerates of smaller particles ($<0.1 \mu\text{m}$ in geometric diameter). The chains are surrounded by shells with lower electron density than the particles in the core. The ESCA analysis of unwashed particles is just valid for the outer layer of these shells. After washing, a large fraction of the shell has been dissolved and information on the core material is obtained from ESCA. The TEM studies have shown that after washing, the core particles consist of smaller homogeneous particles with diameters of about $0.01 \mu\text{m}$. The ESCA results are representative of about 80% of the volume of particles of this size.

The washing procedure separates the readily soluble Cr from less soluble, in a well-defined way. However, from the toxicological point of view, the separation of these fractions is not well-defined, because of the uncertainty of the hygienic significance of differences in the solubilities of various chromium compounds. In a particle of welding aerosol, the chromium is present in a complex environment and the solubility found in the washing procedure may not, in a simple way, be relevant to the solubility of a given chromium compound in the airways.

Chromium oxidation state results for argon gas metal arc welding are quite different from SMAW-results. Only about 2% of the total chromium is soluble and hexavalent and for both the unwashed and washed aerosol samples the concentrations of hexavalent chromium on the particle surfaces are below the detection limit of the ESCA method ($<15\%$).

The results indicate that, although the aerosols from them have lower relative abundances of total chromium, the use of SMAW-methods would imply significantly higher health hazards than the use of GMAW-methods. Switching to the latter methods, however, may not always be possible for technical reasons. Further, when comparing the health hazards of these two classes of welding, other aspects, such as the hazardous gases emitted during welding have to be taken into consideration. In most processes NO_x is formed and in GMAW and GTAW also considerable amounts of the strong irritant ozone (O_3). Discussions or measurements of these gases have been beyond the scope of this study and hence the conclusions about possible health effects of the SMAW, GMAW and GTAW processes reached here do not include the influence of hazardous gases formed during welding.

Within the uncertainties of the differences in welding conditions and parameters, the results about the content and oxidation state of chromium in welding aerosols found here are consistent with those of other studies^{3,2-3,4}.

PARTICLE SIZE DISTRIBUTION

In Table 6 the mass median aerodynamic diameters (MMAD), as determined by the Battelle cascade impactor, are summarized. A typical value of the geometrical standard deviation of the distributions is 1.5. The MMAD-values are calculated from PIXE-analysis of the impactor stages and expressed as the MMAD for each element separately. In the case of gas tungsten arc welding the particles are so small that about 75% of the detected mass is found on the after-filter of the impactor and the MMAD value is thus less than 0.25 μm which is the 50% cut-off diameter of the last impaction stage. The mass median aerodynamic diameters for the other methods vary from 0.3 μm to about 0.6 μm . Hence the particles are respirable and have a high probability of deposition in the lower parts of the

Mass median aerodynamic diameter (μm)

Electrode	F	Al	K	Ca	Ti	Cr	Mn	Fe	Ni
OK 38.65	.34		.32	.36			.33	.33	
OK 38.85			.45				.45	.45	
OK 38.95			.48				.48	.48	
OK 48.00	.48		.50	.44	.50		.46	.44	
OK 61.41			.39	.43	.39	.38	.39	.39	.35
OK 63.35			.39	.39		.39	.39	.42	
OK 69.21						.47	.49	.30	
OK 12.51 ¹							.32	.33	
OK 16.32 ²						.31	.30		.32
OK 16.32 ³						.34	.34	.35	.34
OK 18.01 ²		.42							
OK 18.13 ²		.37							

1) 100% CO₂; 2) 100% Ar; 3) 80% Ar and 20% CO₂

Table 6. Mass median aerodynamic diameter for different elements and welding methods as determined by the Battelle cascade impactor and PIXE analysis.

respiratory tract. In other welding aerosol studies, only a few particle size distribution determinations have been reported. The results of refs. 2,3,4,5,9,27 are essentially in agreement with those of the present study. The low MMAD values found in GTAW indicate that the high arc temperatures in this type of welding (approx. 10000 K) together with the basically non-melting electrode, made from thoriated tungsten, promote the formation of very small particles.

The particles emitted in SMAW-methods contain significant concentrations of highly soluble and hygroscopic compounds derived from elements such as F, K and Na in the electrode coating. The high relative humidity of the human respiratory tract, $RH > 99\%$ in the subglottic region³⁵, makes the particles rapidly absorb water, which may significantly alter the patterns of deposition there.

Particle size determinations have been carried out for all methods and sets of parameters. When the welding parameters are changed, only negligible variations ($<10\%$) of the particle diameter will occur. The variation of the MMAD between elements for a certain method is also negligible. The particle formation process normally includes evaporation, oxidation and condensation steps³. The process has been shown to be sensitive to the welding parameters in producing different compositions and mass concentrations but apparently this is not reflected in the particle sizes, but rather in the number concentration of the aerosols. One important implication of these results is the possibility of using a simplified method to characterize welding aerosols including only a few particle size determinations for each method. The particle size determination is rather tedious and complicated insofar as sampling and analysis are concerned and a reduction in the number of determinations will save substantial time and effort.

SUMMARY

Several welding methods were characterized using a specially designed collection apparatus which has been found to be reliable and to yield accurate and representative sampling of welding aerosols. Special requirements of very low air velocity around the welding place and the possibility of testing the GMAW methods in automatic mode excluded the use of the standardized "Swedish fume box"³⁶. The analytical facility of Particle Induced X-ray Emission was a prerequisite for this extensive and detailed study. The PIXE method, with complementary nuclear methods, is very well suited to the study of work environment aerosols in general¹⁴ and welding aerosols in particular, in that it yields complete quantitative information of many important elements at a low cost. Furthermore, as compared to traditional techniques it significantly simplifies particle size determination.

The highest fume emission in this study is found for SMAW methods followed by GMAW of aluminium and GMAW of steel. By far the lowest emission is found for GTAW of stainless steel. The fume emission rate (E) is determined primarily by the welding current and a similar current dependence is found for all SMAW methods if welded at normal voltage. The voltage also affects E but to a smaller extent. The relative fume formation index (R) varies drastically among the methods and is dependent on the welding parameters. For gas metal arc welding of mild steel with pure CO₂ as the protective gas, R decreases with increasing current.

The composition of the shielding gas in GMAW is important for the fume production. R is higher in the case of the Ar/CO₂ mixture than in the case of pure Ar. The influence of the welding parameters on fume formation is altered by mixing CO₂ into Ar. This study supports the findings of earlier works, viz. that the oxidizing potential of the gas surrounding the electric arc is of considerable importance in determining the fume production, with increased fume production when increasing the oxidation potential of the protective gas.

The elemental composition of a welding aerosol is dependent on the method but also on the welding parameters, primarily the voltage. The fume contains the same elements as does the consumable but with the relative abundances changed due to fractionation effects during aerosol formation. This is explained by the different properties of the elements, e.g. with regard to vapour pressures of the pure elements and their compounds. For SMAW with the recommended voltage,

only minor variations occur when the current is changed. Welding voltage and current mode (AC/DC) have drastic impacts on the elemental composition of the fumes. This is probably due to changes in electric arc length and arc characteristics respectively. The elemental composition of a GMAW aerosol is also dependent on the protective gas. Thus, a relative decrease in several elements is noted when the transition from globular to spray transfer takes place in an Ar atmosphere. The complexity of fume formation processes and the growing popularity of GMAW methods in industry due to increased production and welding quality stresses the need for further studies within this field.

The fumes produced from SMAW and GMAW methods when welding stainless steel clearly show the great differences between these two main types of welding procedures. While the chromium in the SMAW aerosols is almost entirely hexavalent (and soluble), only trivalent chromium is found in the GMAW aerosols. The well-known difference in biological activity between the two oxidation states of Cr is reason enough to infer that, if possible, GMAW methods should be chosen when welding stainless steel.

The particles in the welding aerosols are below $1\text{ }\mu\text{m}$ in diameter and consequently respirable and able to reach the lower parts of the human respiratory system. Mass median aerodynamic diameters vary from well below $0.25\text{ }\mu\text{m}$ to $0.6\text{ }\mu\text{m}$ and seem to be rather independent of the welding parameters. An important factor in evaluating the deposition of aerosols from SMAW methods is the hygroscopicity of the particles which, in the high humidity of human airways, may cause changes in the aerodynamic properties of the particles.

ACKNOWLEDGEMENTS

We are indebted to Dr F. Brundin for many stimulating discussions throughout this work and for putting welding equipments and other resources at our disposal. The skilled and patient welding of hundreds of welding joints by Mr. Alex Simonsson is gratefully acknowledged as is much good advice throughout the course of this study.

We have highly appreciated the equipment built by Mr Knut Sjöberg throughout this investigation.

This investigation has been supported financially by the Swedish Work Environment Fund.

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